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PROGRESS REPORT

of the

SOUTHERN UTILIZATION RESEARCH AND
DEVELOPMENT DIVISION

AGRICULTURAL RESEARCH SERVICE

This progress report includes a summary of the current research of the Division and a preliminary report of progress made during the preceding year. It is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

The summaries of progress on USDA and cooperative research include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed, will be released promptly through established channels. Because of this, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a list of publications reporting results of USDA and cooperative research issued between April 1, 1968, and March 31, 1969. Current agricultural research findings are also published in the monthly USDA publication, Agricultural Research. This progress report was compiled in the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana 70124.

UNITED STATES DEPARTMENT OF AGRICULTURE

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INTRODUCTION

Organization of the Division

The Southern Utilization Research and Development Division currently conducts research on cotton, cottonseed, peanuts, citrus and subtropical fruits, rice, sweet sorghum, naval stores, cucumbers, sweetpotatoes, and other vegetables. The program includes basic and applied research in the physical and biological sciences and engineering. Basic research plays a key role in uncovering new information that later may be exploited in applied research and development. When appropriate, engineers carry out pilot-plant studies of promising laboratory developments to provide engineering and cost data essential to determining feasibility for industrial application. Division scientists consult with specialists from other organizations during both the planning and the execution of the research, and cooperate actively with industry to facilitate commercialization and utilization of new findings.

The Division's research staff is organized into nine commodity-oriented Laboratories (Cotton Finishes, Cotton Chemical Reactions, Cotton Mechanical, Cotton Physical Properties, Textiles and Clothing, Oilseed Crops, Food Crops, Fruit and Vegetable Products, and Naval Stores), and one Laboratory (Engineering and Development) for engineering research and development.

Headquarters of the Division are located at the Southern Regional Research Laboratory, New Orleans, Louisiana. The Division also has personnel and laboratory facilities at Winter Haven and Olustee, Florida; Weslaco, Texas; Raleigh, North Carolina; Knoxville, Tennessee; and Natick, Massachusetts.

Examples of Outstanding Accomplishments

All-Cotton Durable-Press Seersucker Garments Regain Markets for Cotton. All-cotton seersucker is unquestionably the most comfortable dress wear for men during the hot summer months. However, wrinkling and bagging of the material together with the need for frequent and expensive commercial laundering long ago deprived cotton of this very valuable market. Recognizing the relation of fabric design to performance, Department scientists in cooperation with the Cotton Producers Institute developed a new all-cotton durable-press seersucker fabric with the desired properties of comfort, appearance, and durability. After an outstanding success in market tests sponsored by the National Cotton Council, men's suits made from this fabric were produced commercially, advertised as "the Memory Suit that never forgets its shape." They proved so popular that orders from merchants far exceeded production. Commercialization of men's wear was soon followed by marketing of women's and children's apparel, equally comfortable and durable but produced in brighter colors and with modified fabric structure to attract the target consumers. Twofold benefits should accrue to cotton: The potential market for all types of seersucker garments is conservatively estimated to be 78,500 bales of cotton annually.

And, since the basic findings are applicable to many types of fabrics, the improved seersucker suit may herald the appearance of other all-cotton suits, such as corduroys and tropicals.

SRRL Bale-Opener-Blender Being Commercialized After Successful Mill Trials. One of the most promising textile machines yet developed by Department scientists is the Bale-Opener-Blender (BOB). The first commercial model is being manufactured by one of the three current licensees. The BOB actually surpassed its design capability during recent large-scale evaluation tests in a commercial mill. These tests proved that although it was designed to have a production rate of 1,000 pounds per hour, it was in fact capable of processing 1,400 pounds per hour continuously and 2,000 pounds per hour intermittently--many times the production rate of conventional blenders. In addition to its speed, the BOB has many other advantages. It reduced the number of bales required in a mix from 43 to 20. It replaced seven machines used in a three-picker opening line. Its feed control compensates for irregularities in size and density of the bales and renders the machine completely automatic except for loading. But the ultimate criterion, of course, is the quality of fabric produced from the blended cotton, and here the BOB excels: the resulting fabric was 20% higher in grade than that produced from cotton processed by the conventional system. Because of these features, use of the BOB will reduce costs an estimated one-fourth cent per pound of cotton processed: for each million bales of cotton processed, the cotton textile industry can save $1,250,000.

Cottonseed Protein Concentrates and Isolates Developed for the Enrichment of Food Products. If present trends in the United States continue, markets for edible vegetable proteins are expected to increase manyfold within the next five years: from 30 million to 275 million pounds of concentrates (at least 70% protein) and from 20 million to 225 million pounds of isolates (at least 90% protein). The advent of glandless cottonseed--some 10,000 tons have been contracted for at a premium price--creates a special opportunity for edible cottonseed protein products. A protein concentrate and two isolates that USDA scientists recently prepared promise not only to improve cottonseed's competitive position in domestic markets but also to contribute toward easing the growing problem of protein malnutrition in developing countries. The concentrate is conveniently prepared from defatted cottonseed flour by the dry operation of air classification, which can be carried out on commercial equipment. The isolates--one composed of the low molecular weight, water-soluble proteins, the other of the high molecular weight, acid-soluble storage proteins of the seed--are obtained by a two-step extraction procedure, which has been successfully transferred to pilot-plant scale in cooperation with a large food processor. Cottonseed concentrate and isolate have been evaluated in bakery items and in comminuted or simulated meats. In sponge and dough bread formulations, they could be used to replace

nonfat dry milk or to produce very good high protein bread. Frankfurter preparations containing the cottonseed products had excellent flavor and good fat absorption. The unusual property of acid solubility makes one isolate particularly valuable in the preparation of certain protein-fortified beverages, such as citrus drinks.

Filterability Test Now Used in Grading Most of the Raw Cane Sugar Imported into the United States. Several years ago, Department scientists developed a filterability test for cane sugar: it was sensitive, reproducible, rapid, and inexpensive, and the results correlated well with performance during refining. Because of these superior properties, the test is now used to predict the refining quality and thus the price of most of the raw cane sugar imported into the United States--annually about four million tons worth $500,000,000. If the filterability as determined by the test falls outside certain limits, penalties are subtracted or premiums added to the price of the sugar. In fact, the inclusion of the filterability test among the procedures used to assess quality is now required as part of the import contract. In addition, domestic sugar manufacturers report that they use it in quality control, such as evaluating or improving the efficiency of certain processing operations. It is also widely used abroad in plants producing sugar for sale to the United States.

AREA 1 - COTTON UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
407	New and improved feed, textile, and industrial products from field crops			
	Chemical composition, physical properties, and structure	21.9	0.9	22.8
	Chemical and physical investigations to improve products	25.0	1.5	26.5
	Technology--process and product development	53.8	5.9	59.7
	Subtotal	100.7	8.3	109.0
705	Selection and care of clothing and household textiles			
	Chemical and physical investigations to improve products		0.5	0.5
	Subtotal		0.5	0.5
709	Reduction in health hazards involved in use of nonfood farm products			
	Chemical and physical investigations to improve products		1.0	1.0
	Technology--process and product development	10.9		10.9
	Subtotal	10.9	1.0	11.9
	TOTAL	111.6	9.8	121.4

Domestic program supplemented by P.L. 480 funds in 8 countries totaling 282,633 U.S. dollars equivalent per year (India, Israel, Belgium, Holland, Spain, Sweden, Switzerland, England).

Problems and Objectives

Synthetic or "manmade" fibers have aggressively encroached on cotton's markets, gradually reducing its share of the total U. S. mill consumption of textile fibers to less than forty percent. In addition, U. S. capacity for producing cotton can far outpace consumption; even with acreage restrictions, production has frequently exceeded domestic consumption plus exports. Compounding these problems is the fact that some of the crop consists of lower quality cottons that are too difficult and expensive to process into commercially acceptable products. To help solve these problems, utilization research is directed toward the development of fundamental information and technology required for the production of new and improved cotton products to retain present markets and open new ones for this natural fiber.

Major objectives of the research are to develop:

1. Fundamental knowledge of the composition, structure, and properties of native and modified cottons.

2. New or improved techniques and machinery for mechanical processing of cotton.

3. Chemical and physical modifications and treatments to create new or improved cotton products for various end uses.

4. Flame-retardant cotton products to help protect the consumer and reduce loss of property from fire.

5. Improved laundering procedures to minimize or eliminate microbiological contamination of textile products.

Progress - USDA and Cooperative Program

RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL PRODUCTS FROM FIELD CROPS

A. Chemical Composition, Physical Properties, and Structure

1. Relationships of the Structural Arrangements Within Cotton Fibers to the Physical and Chemical Properties of Native and Modified Cottons. Electron microscopical studies by the methacrylate embedding technique indicated that partially etherified cotton fibers have a structure different from that of the partial esters. The average refractive indices of esters with aromatic groups are higher than those of esters with aliphatic substituents. Cupriethylenediamine hydroxide (cuene) solubility patterns were determined on ultrathin cross sections of cotton fibers from fabrics crosslinked by vapor phase processes using various crosslinking agents and different catalysts. For most samples, there were indications that the

reaction had occurred only in the periphery of the fiber. Notable exceptions were the samples reacted with paraformaldehyde and formic acid catalyst to approximately 1% formaldehyde content in which reaction apparently occurred throughout the fiber cross section. This research is providing new knowledge about ultrastructure and properties of chemically treated cottons.

The spiral angle of fibers from ten different varieties of cotton representing three genetic species was found to be a constant value of approximately 22° regardless of genetic origin. It was further shown that this constant angle of spiral is involved in the X-ray and optical measurements of orientation but masked by the convolutions present within the fibers. The results indicate that the classical methods of measuring orientation within cotton fibers, i.e. X-ray diffraction or optical birefringence, are distorted by the convolutions present in the fiber to the extent that both techniques are in effect measuring the amount of convolution-distortion rather than true molecular or crystallite orientation.

Microscopical and X-ray determinations are underway to determine dispersion of crystallites around the fibril axis, and the gross alignment of fibrils and of crystallites with respect to the fiber axis, in native and modified cottons. Changes in subfiber morphology and in microporosity caused by chemical modification for durable press will be followed by electron microscopy and nitrogen-sorption techniques.

Cotton yarn activated by benzyltrimethylammonium hydroxide showed much greater reactivity in etherification with organic halides than if the yarns were activated with sodium hydroxide. This confirms the greater effectiveness of the former agent as a swelling and decrystallizing agent for cotton. The resulting cellulose ethers appeared to be largely amorphous while wet with the swelling agent, but they recrystallized during washing and drying of the yarns. The degree of orientation was increased by tensioning during drying. The yarn strength also increased greatly in tensioning, becoming greater than the strength of the original untreated yarn. The tension developed in cotton yarn treated at constant length with various swelling agents has been measured and appears to depend on the amount of cellulose swelling that occurs. Addition of sodium thiocyanate to sodium hydroxide increased the effectiveness of the latter as a swelling agent for cotton, and may be useful in mercerization processes.

Cotton fibers grown under seven different temperature schedules had increasing X-ray crystallinities and orientation angles as growth of the boll proceeded. After boll opening, crystallinity did not show a consistent trend with average growth temperature but orientation angle tended to decrease with increasing temperature. Accessibility of the cellulose, as indicated by enzymolysis, dye and iodine sorption, and deuterium oxide exchange, decreased with increasing age of boll, showing a marked decrease after boll opening. Dye and iodine sorption tended to be higher for fibers grown at the lower temperatures. This information is useful in predicting properties of cotton

harvested before bolls have completely matured or of late-season cotton grown during cooler days and nights. Higher accessibility resulting from either immaturity or low growth temperatures would cause higher dye uptake and a different reaction to resins and other chemical finishing treatments applied to textiles.

In P. L. 480 research at the University of Ghent, Belgium, a survey for presence of reversals in twenty wild-type species of Gossypium showed that most of them had none. One group had about 10 reversals per centimeter. Only those closely related to cultivated species had many (18 to 28 per centimeter). Within variety, the reversal frequency was so remarkably constant that it could be used to distinguish one kind from another. Mechanical and chemical treatments did not change reversal frequency. Measurement of fiber strength at and close to reversals showed that the weak point is really a weak zone. Tests to determine whether the strength between reversals is different for S- and Z-spiralled fiber sections were inconclusive and will be repeated. Test conditions or treatments that change fiber strength--relative humidity, mercerization, bleaching, heating, steaming, enzyme action, DMEU-crosslinking, gamma radiation--appear to affect the strength at and between reversals nearly to the same extent. A very high correlation exists between strength at and between reversals, and between these and the Pressley bundle strength at zero and 1/8" gauge length.

An investigation of the fundamental mechanisms and bonding forces that could be used to improve the physical properties of cotton textiles was continued in a P. L. 480 project at the Fiber Research Institute, T.N.O., Delft, Holland. The researchers determined the effect of conditions of temperature, moisture, and degree of tensioning of cotton yarns and fibers during swelling in different swelling agents on tensile strength, elastic recovery, and other mechanical properties. The data indicated that optimum elastic recovery is obtained with a relatively disordered structure achieved by slack swelling in strongly alkaline media. High total strength resulted from treatments that afforded well penetrated, highly ordered structure. Cottons swollen to different degrees, then solvent exchanged to remove caustic and water were crosslinked in the dry state with diacid chlorides of varying chain length and the physical properties of the crosslinked cottons compared with those of control samples. Results not yet completely analyzed indicate that data on fibers are more informative than those on yarns because of factors affecting interfiber friction in the yarns.

The influence of yarn geometry on the response of the structural elements of chemically treated cottons to stress and deformation is being studied in P. L. 480 research at the Central Laboratory, T.N.O., Delft, Holland. All preliminary work on untreated and scoured yarns of various twist multipliers has been completed, and an investigation of chemically treated counterparts of these materials is in progress.

2. Adsorption and Swelling Phenomena in Native and Modified Cottons. Significant differences were found in surface areas (or extent of swelling) of cottons treated with reagents used in several methods for crosslinking cotton fabrics with formaldehyde in the wet state. Although the inclusion of the crosslinking agent always reduced the area found in samples treated in the solutions of the swelling agent only, preswelling followed by immersion of the undried sample in the crosslinking solution conserved a large amount of the surface. The increase in surface area in all but one swelling treatment was in pores of approximately 40 angstroms or less in diameter (or width). These findings indicate that studies of gas adsorption at liquid nitrogen temperatures by samples exchanged from treating solutions through appropriate reagents to helium can evaluate comparative changes in the microporous structure of cotton fibers while being processed in liquids.

In formaldehyde-crosslinked cottons, the caustic sorptivity (as measured by the alkali centrifuge value - ACV) usually decreases with increasing formaldehyde content. The crosslinks restrict the swelling of the fibers in the 15% sodium hydroxide solution so that the sorptive capacity is decreased and the ACV lowered. An exception to this trend was found for samples in which low percentages of formaldehyde (about 0.25%) were introduced into water-swollen fibers; in these, the ACV's increased (about 17%) over the value of the uncrosslinked control. In our earlier work with the alkali centrifuge tests, an increase in ACV was considered to be indicative of fiber damage. However, in these crosslinked samples, any degradative action that might be attributed to the components of the media was found to be relatively minor and did not account for the large increase in ACV mentioned above. Therefore, a rearrangement of intrafiber structure must occur during crosslinking under these conditions to accommodate the volume of caustic solution represented by the increase in ACV.

If caustic solutions of different strengths are used in the alkali centrifuge procedure when testing crosslinked cottons, the strength of the caustic solution needed to produce a selected degree of swelling is indicative of the relative restraining powers of the crosslinking networks. The caustic sorptivity (as measured by ACV) tends to decrease with increasing crosslinks in samples prepared by the pad-dry-cure method. The stage from which the sample is taken in the dual-step polyset method of treatment also affects the caustic sorptivity.

Research investigations of the physical chemistry and thermodynamics of solution and vapor phase adsorption on and in the cotton fiber were continued in a P. L. 480 project at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India. It was found that formaldehyde-treated cotton (Form D) decrosslinked by acid hydrolysis adsorbed more dye than did native cotton treated similarly with acid. As determined by an extrapolation to saturation value, the amounts of combined formaldehyde in Form D and Form W cottons were identical and agreed with a calculated value based on the assumption of monomeric crosslinks in a cotton of 70% crystallinity.

Form W and Form D cottons had equilibrium isotherms which followed the Langmuir equation within certain concentration ranges. Standard free energies differed but were small positive values for both forms. The amount of primary bound water and the ΔH^* of activation for its removal differed in Form D and Form W cottons and differed from the respective values for native cotton.

In P. L. 480 research at the Shri Ram Institute for Industrial Research, Delhi, India, further progress has been made on a study of the moisture sorption and desorption by crosslinked cotton over the entire humidity range as related to the state of swelling under which the cellulose is crosslinked. Crosslinking with formaldehyde has been extended from fiber samples to fabric samples, and fabric properties have been determined. Crosslinking has also been done with epichlorohydrin, 1,3-dichloropropanol, divinylsulfone, bis-(2-hydroxyethyl)sulfone, dimethylethyleneurea, and dimethylolurea. Water imbibition values have been obtained on selected samples. It has been postulated that the primary wall breaks at 19% swelling under acid conditions. This provides an explanation for the behavior of samples crosslinked with formaldehyde under these conditions.

3. Mechanisms of Physical Damage to Cotton By Mechanical, Chemical, Physical or Biological Actions. An investigation of the nature and mechanism of the chemical effects of ultraviolet light on cotton cellulose and related compounds is continuing under a P. L. 480 project at the University of Salford, Lancashire, England. Now being studied are the mechanisms and kinetics of reactions involving the anthraquinonoid group of vat dyes, which actively sensitizes the photo-oxidation of cotton. The role of sodium 9,10-anthraquinone-2-sulfonate in photo-oxidation in aqueous-alcoholic solutions was investigated by flash and continuous photolysis and electron spin resonance techniques. Mechanisms by which the photo-excited quinone reacted in aqueous and in aqueous-alcoholic solutions were elucidated. Two reaction paths were identified: (1) destruction of the sensitizer, and (2) photodegradation of the carbohydrate. Irradiation of sensitized cotton cellulose with light of 3650 A. led to a decrease in its degree of polymerization which varied linearly with the concentration of adsorbed sensitizer (anthraquinone-2-sulfonate). The effects of oxygen and water vapor on this process were examined. The degradation of cellulose occurred by a proton abstraction mechanism. Semiconductivity measurements on photo-excited carbohydrates were continued.

In a P. L. 480 project at the University of Bombay, India, research is in progress to investigate the inhibition of the photochemical degradation of cotton by chemical modification and deposition of inorganic and organic compounds. It has been found that partially benzoylated cotton shows protection against degradation by sunlight, but partial benzylation accelerates degradation. Humidity greatly influences the extent of degradation. Hydroxides, phosphates, and silicates of manganese, nickel, cobalt, cadmium, aluminum, and chromium have been applied to cotton fabric at levels of 0.5% and 1.0%.

Only the hydroxides and phosphates of nickel and manganese afforded protection against sunlight. The 0.5% and 1.0% levels of the same compound did not give significantly different protection.

4. Structural and Compositional Changes Occurring During Chemical and Physical Modification of Cotton Cellulose. The infrared spectra of cellulose and of modified celluloses were examined, and techniques were devised to obtain polarized spectra of films prepared from parallelized fibers in an effort to correlate the absorption bands in the 700-300 cm^{-1} region of the spectrum with the molecular structural changes produced by the modification of cotton. Preliminary results indicate that bands at 660, 520, 455, 430, 358, and 335 cm^{-1} in the spectrum of cotton are associated with OH vibrations and hydrogen bonding effects and that molecular orientation may be the same for mercerized and unmercerized cotton. A method of identifying softeners, sizes, and lubricants that increase the abrasion resistance of cotton fabrics has been developed. It appears that some of these additives may increase abrasion resistance by reacting with the cotton. Knowledge of the changes in molecular structure of modified cotton, as well as of the effect of softeners and other additives on the fabric, will be useful to the industry in the development of improved durable-press products.

The accessibility of the cellulose in cottons treated to various extents with formaldehyde by different processes and with other intermolecular crosslinking agents has been evaluated by the changes in crystalline character. induced by exposure to swelling agents. A computer-programmed X-ray diffraction analysis was used to determine the extent of conversion to new lattice form or disordered state in the cellulose polymer. Sodium hydroxide solutions of mercerizing strength (20% or greater) produce a limiting degree of disordered cellulose (about 65%) in all specimens, without loss of bound formaldehyde. Less cellulose II is formed when the cellulose is crosslinked more extensively, particularly when weaker alkali solutions are used as the swelling agents. Crosslinks formed in the unswollen cellulose (vapor phase treatments) tend to reduce accessibility to swelling agents more than do those introduced from liquid systems.

A technique has been developed to correct for instrumental errors in nuclear magnetic resonance (NMR) signals obtained from cotton. Investigation of line shape parameters for a variety of crosslinked cotton fabrics involving four crosslinking agents and add-on of .06 to 2.37% formaldehyde showed no significant differences among the samples. Data relating the crystallinity of celluloses and the second moments of their NMR spectra have been obtained. A technique that gives a quantitative measure of the number of protons in various sorption states of water-cellulose sorption systems was also developed. The importance of understanding the liquid-cellulose sorption mechanism is indicated not only by the well-known influence of sorbed water on the physical properties of cotton but also by the fact that many technological processes in the cotton industry involve exposure of cotton to water or other solvent solutions and vapors.

An investigation of the reversible reaction of methyl vinyl sulfone with cotton cellulose has shown that this reaction is influenced by temperature, base concentration, and physical state of the cotton. Reaction at a specific hydroxyl group is controlled by a complex interplay of its rate of reaction and its availability to the reagent. Temperature has an accelerating effect on reaction rate, whereas increasing base concentration affects the relative reactivities of the various hydroxyl groups. The physical state of the cotton affects the reaction in such a manner that both rate of reaction and accessibility of hydroxyls decrease from cotton cellulose in solution to decrystallized cotton to fibrous cotton. Properties of cotton crosslinked with divinyl sulfone in the presence of base concentrations varying from 0.1N to 4.0N indicate greater penetration of reagent into the microstructure of the cotton with increasing base concentrations. This appears to result in increasing amounts of long crosslinks, graft polymer and deposited polymer within the microstructure and is reflected by the physical properties of the crosslinked fabrics.

The relative distribution of diethylaminoethyl groups at the 2-O-, 3-O-, and 6-O-positions of cotton resulting from heterogeneous reactions in media of various base concentrations and in homogeneous solution has given a measure of the relative reactivities of the different hydroxyl groups and the effect of base concentration on the accessibilities of the different types of hydroxyl groups in cotton cellulose. The reaction of sodium 2-aminoethyl sulfate with cotton resulted in a product that upon hydrolysis yielded O-(2-aminoethyl)-D-glucoses, polyethylenimines, and ethanolamine in the ratio of 0.5:0.4:0.1. This indicates that only 50% of the modifying agent developed ether linkages. The actual degree of substitution of cotton modified with tris(1-aziridinyl)phosphine oxide (APO) was estimated to be 0.0098 for an APO incorporation of 15%, suggesting that extensive reaction of resin-forming chemical modifying agents is not essential for the development of wash-wear properties.

A novel gel permeation technique, previously developed for measurement of changes produced by modification of decrystallized cotton, has been modified and applied to samples ground to a suitable size for filling chromatographic columns without significant alteration of crystallinity. Determinations of relative internal volumes, and of limits of permeability to solutes of known sizes, afford a unique means of relating alterations of fabric properties to changes in the molecular structure of the cellulose polymer produced by various chemical treatments. Formaldehyde crosslinking in a nonswelling reaction medium reduced the accessible internal volume by 50%, while reducing the molecular weight limit of permeability to approximately 40% of that found for unmodified cotton. Measurements by this new technique showed that formaldehyde crosslinking tends to fix the fiber polymer in the state of collapse or swelling attained during the time that it is subjected to various reaction conditions.

A research study of the chemistry and structural nature of the bonds formed between formaldehyde and cellulose in formaldehyde-treated cottons has continued in a P. L. 480 project at the Swiss Federal Institute of Technology, Zurich, Switzerland. A new method was developed for complete permethylation by use of an exchange methylation method following prior methylation by a standard technique. A new and superior method was also developed for isolating and purifying the methylation products by dialysis. Other minor improvements have also been made in the analytical techniques for determining structural features of cotton crosslinked with formaldehyde, preparatory to applying the revised methods to cotton compositions containing normal (i.e., relatively small) amounts of bound formaldehyde.

In a completed P. L. 480 research project at the Shirley Institute, Manchester, England, chemical evidence has indicated that the elementary structural units in cotton cellulose are of the same general dimensions as those observed in electron microscopy. Only certain hydroxyl groups occupying three positions in the anhydroglucose unit of cellulose are available on the surface of the elementary structural unit to reactants. A more quantitative relationship was provided to explain the penetration of the cellulose unit as a function of reaction conditions. Methylation of crosslinked cotton fabrics did not greatly alter physical properties. Ethylation produced changes in accessibility differing from those resulting from methylation. Hydroxypropylation as crosslinking pretreatment increased wet and dry resilience, but lowered strength and abrasion resistance. Crosslinking benzyl celluloses reduced wet and dry resilience at high degrees of benzyl substitution.

In other P. L. 480 research at the Shirley Institute, a study was previously made of the fine structure of scoured Acala 4-42 cotton treated with 5N sodium hydroxide at various conditions of temperature, washing, and drying. Investigations of swelling by other agents have now been completed. The effects of nitric and perchloric acids, inorganic salts, and usual cellulose solvents were measured by changes in fiber width, moisture regain, water retention, metaperiodate oxidation, X-ray diffraction pattern, acetylation rate, extent of acid hydrolysis, and density. General conclusions were that high reactivity depends on whether inter- or intrafibrillar swelling occurs, rather than on degree of swelling. Swelling by acids and salts is promoted by higher temperatures and prolonged treatment. In general, swelling occurs over two distinct concentration ranges (inter- and intrafibrillar swelling) but each reagent has some feature different from the others. Methylation and acetylation were shown to be useful for measuring internal surface of swollen cottons.

5. Relationship of Gross Structure of Cotton to Behavior of the Fibers in Textile Structures. In a recently completed P. L. 480 project at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, an improved instrument for electronically measuring the hairiness of cotton yarns was used to study the effect of fiber properties and mechanical

variables on yarn hairiness. Total hairiness was shown to increase with decreasing fiber length, decreasing Micronaire reading, and increasing short fiber content. For a constant traveler weight, hairiness increased slightly with increasing spindle speed. Coarse yarns were more hairy than fine yarns. The Casablanca drafting system yielded less hairy yarns than other systems evaluated. Combed yarns were less hairy than carded yarns spun on conventional systems, and were similar to carded yarns spun on an "open-end" system. Yarns spun on the Platt-Shirley miniature spinning system were comparable in hairiness to those spun on conventional systems.

6. Methods and Instruments for Measuring the Physical Properties of Cotton and Its Products. Research to correlate abrasion tests with service wear of durable-press cottons has continued. It has been found that the surface condition of the dryer drum can cause more edge abrasive damage to all-cotton durable-press fabrics laundered in home laundering equipment than the actual drying temperature used in the drying cycle. Changes in physical properties of these fabrics due to laundering appear to be the same regardless of: (a) whether the wash load is composed of mixed fabrics or the same type fabric; (b) whether the dryer used is old, new, electric, or gas; and (c) the drying conditions used, for example, line-dry, under-dry, normal-dry, or over-dry. Abrasion damage is significantly affected by (b) and (c). In-service evaluations of abrasive wear for different wearers show patterns different from each other and none show any apparent agreement with laboratory tests. Results also show disagreement with laboratory abrasion tests, including tests performed in home laundering equipment. Agreement was found between some laboratory abrasion tests while no agreement was found between others. Physical properties other than abrasion generally showed no correlation with abrasive wear for the fabrics studied. This is possibly due to the small differences found in the physical properties between the different treatments for each fabric.

Additional fundamental research on the geometry of wrinkles as they affect the rating of acceptability of wash-wear cotton fabrics was conducted in a P. L. 480 project at the Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry of the State of Israel. Principles of light slit illumination, pneumatics and voltage transducers were used in developing three different methods of describing a wrinkled fabric surface. The light and pneumatic means have proven unsuccessful. The transducer means is presently under investigation. Attempts to measure the forces and energies involved in forming wrinkles by extending fabric strips proved unsuccessful. Examination of the stress-strain relationships of fabric strips of different lengths and widths, with and without wrinkles, showed that measurement of this relationship was not possible over the whole range of the stress-strain curve.

In completed contract research at Stanford Research Institute, South Pasadena, California, a prototype instrument for counting neps in cotton has been developed, based on the measurement of light reflected from neps as compared with light reflected from individual fibers. The instrument is

somewhat hampered by a tendency to count both neps and particles of trash; nevertheless it will be a worthwhile research tool. The technique has potential for application to counting discrete particles, a problem found in many areas of research and manufacturing.

The same contractor (Stanford Research Institute) has also evaluated the major part of a new instrument for measuring fiber length and length distribution. The mechanism for exposing a predetermined number of straightened cotton fibers to the measuring element is being assembled after much delay in obtaining optical components. Preliminary evaluation indicates a measurement rate of 300 fibers/minute, one-half the desired rate. The counting and readout system is being assembled.

Researchers at the Lodz Polytechnic College, Lodz, Poland, have completed P. L. 480 research studies of the mathematical and theoretical aspects of the relationship between fiber-length distribution in cotton specimens before and after sample preparation. Models for fiber breakage and the related basic mathematical expressions were developed. Experimental investigation to obtain verification was conducted using already existing data on cottons that had been extensively studied at the Southern Division. In considering the effect of taper in cotton fibers, the data obtained suggest that taper is important in fiber breakage in the early phases (carding) of textile processing. In later stages (postcarding) the fiber breakage that occurs more nearly fits the hypothesis of a cylindrical fiber. Another important model took into account the effect of waste or noil removal.

B. Chemical and Physical Investigations to Improve Products

1. Exploratory Chemical Modification and Finishing of Cotton. A commercial mixture of chlorinated and nonchlorinated triphenylsulfonium chlorides was found to react with cotton yarn in the presence of aqueous sodium hydroxide to yield a crosslinked cationic cellulose derivative containing sulfur. Practically no reaction occurred between pure triphenylsulfonium chloride and cellulose under the same conditions, indicating chlorinated triphenylsulfonium salts were the cellulose-reactive components. These may have served as a new type of cellulose arylating and crosslinking agent. Treatment of cotton with hydrazine and hydrogen peroxide was found to cause fairly rapid decomposition of cellulose to soluble products, thus permitting analysis of cotton-polyester blends. A new compound synthesized as a potential cellulose crosslinking agent was dipotassium 1,4-bis(thiosulfatomethyl)benzene. The rate of graft polymerization of vinyl and acrylic monomers on cotton fabric was accelerated greatly by prior phosphorylation of the cotton, and may lead to new delayed curing processes for durable-press finishing.

Cotton cellulose dicyclopentadienemonocarboxylate fabrics showed a large increase in wrinkle recovery as a result of the dissociation and recombination of the substituent groups when the fabric was heated for extended

periods. This constitutes a novel uncatalyzed delayed-cure process for crosslinking cotton cellulose. The rate of the dissociation reaction in collapsed fibers was slower than in swollen fibers. Cotton cellulose fabrics crosslinked with dicyclopentadienedicarboxylic acid could be sharply and durably creased by extended heating of the folded fabric. The creases could be removed by further heating of the unfolded fabric, thus proving the thermally reversible nature of the crosslinks. Cotton cellulose fabrics containing quaternized diethylaminoethyl substituents in the hydroxide form were found to be internally catalyzed substrates for crosslinking with divinyl sulfone. The crosslinked fabric attained high wrinkle recovery when re-cured at 160°C. The study of this novel type of delayed cure process was extended to the reaction of divinyl sulfone with fabrics prepared by the reaction of cotton cellulose with 3-chloro-2-hydroxypropyltrimethylammonium hydroxide under mercerizing conditions.

The investigation of the thermal dissociation of unsubstituted N-phenylcarbamylated cotton prepared by the treatment of cotton fabrics with phenyl isocyanate or with phenyl carbanilate has been completed. Vacuum isothermal and dynamic thermogravimetric analysis and differential scanning calorimetry were used to calculate kinetic and other thermal data. This work has led to the postulation that two concurrent decompositions occur: a rapid cellulose N-phenylcarbamate decomposition and a slower cellulose N,N'-diphenylallophanate decomposition. The results of thermal analyses for carbamylated celluloses demonstrate the presence of a rather complex system that does not resolve into simple thermally reversible linkages suitable for thermally reversible crosslinking systems.

A thermogravimetric analysis (TGA) and differential thermal analysis investigation of samples of 2-, 3-, and 4-pyridylated cotton fabrics was initiated. The initial onset of dissociation of the cellulose pyridylcarbamates occurred at temperatures well below the decomposition temperatures of cellulose itself. The kinetics of the dissociation, as measured by TGA, suggest an intramolecularly catalyzed decomposition reaction for the 2-derivative. This lends support for the expectation that intramolecular catalysis can be utilized in the development of a commercially feasible thermal reversible crosslink system in cotton.

In recently completed grant research at Textile Research Institute, Princeton, New Jersey, the anionic graft polymerization of acrylonitrile on cotton yarns by treatment of sodium cellulosates has been accomplished with no apparent degradation of the cellulose. Only low levels of grafting modification were investigated. There is some evidence of improved thermoplastic character, although there are no apparent changes in the thermal properties attributable to the grafting as revealed by differential thermal analysis.

Cottons with built-in catalytic sites--for example, diethylaminoethyl cottons--have been reacted with various heterocyclic compounds or their precursors to produce cottons whose properties differ from those imparted by

a given heterocyclic in the presence of an external catalyst. In situ catalysis in nonaqueous media yields cottons possessing properties different from those obtained in aqueous media and allows reaction of cellulose with many agents not reactive in aqueous media. If the removal of water is an important part of creaseproofing cotton, reaction in nonaqueous media should be more efficient than reactions in water.

In completed contract research at Bjorksten Research Laboratories, Madison, Wisconsin, cotton fabric that possesses a combination of high wrinkle recovery, good abrasion resistance, and high strength retention has been prepared by simultaneously applying a thermoplastic polyacrylate and a thermosetting dimethylolethyleneurea monomer and controlling the migration of the resins during the course of drying. The rate and effectiveness of migration is temperature dependent. Below 100°F. the thermosetting resin tends to collect near the periphery of the fibers, and the thermoplastic resin on the surface of the fibers; thus the core of the fibers is essentially devoid of resin. The net result is high crease recovery angle contributed by both the thermoplastic and thermosetting resins, high abrasion resistance due to the surface location of the thermoplastic resin, and high tensile strength as a result of the unreacted core. The order of application plays a large part in the properties of the products.

A number of polymers produce increased abrasion resistance, wrinkle resistance, and smooth-drying properties when applied to the surface of cotton fabrics. However, there is only a very limited knowledge of the principles upon which these materials function to produce these improvements. Such knowledge is being sought in recently initiated contract research at Gulf South Research Institute, New Orleans, Louisiana. In the first phases of the work, tensile and elastic behaviors of films cast from selected polymers are being determined. These, in turn, are being compared to the response of cotton treated with these polymers.

In further contract research at New York University, Bronx, New York, to investigate polymer encapsulation of cotton fibers, vapor phase polyoxymethylene-coated cotton fabrics were treated with various cellulose crosslinking agents in order to enhance their resilience while maintaining other desirable properties, particularly strength and abrasion resistance. Treatment with a typical crosslinking agent, dimethylolethyleneurea, resulted in enhanced wrinkle recoveries together with strength retentions of approximately 80%; preliminary abrasion data are also promising.

Contract research at Harris Research Laboratories, Rockville, Maryland, to develop finishes to make cotton fabrics more rapid drying has been completed. A variety of hydrophobic additives were applied to cotton fabric in conjunction with or subsequent to durable-press treatments. The water imbibition and drying time of treated fabric were determined as a function of additive concentration. In all cases, the water imbibition and time required for drying went through a minimum at relatively low concentrations of additive.

The position of these minima bore little relation to the water- or oil-repellency of the treated fabrics. In some instances, the drying rate was constant over a considerable period of time, while with other treatments the drying rate continuously decreased with time. The time required for drying was a function both of water imbibition and of evaporation rate. This rate depended not only on rate of water transport from fiber, yarn, and fabric interiors to the fabric surface but also on the continuity of surface finishes through which the water had to travel. The drying time of cotton fabric was reduced by 50%-66% in the more effective treatments.

2. Chemical Reactions Initiated in Cotton Cellulose and Chemically Modified Cotton by High-Energy Radiation, Light, and Heat. Elucidation of the fundamental principles of free radical reactions of cotton cellulose initiated by high-energy radiation, light, complexes, and hydroxyl and perhydroxyl radicals generated by redox systems showed that the two-step radiation-initiated copolymerization reactions of cellulose were probably the most feasible free radical reactions for the preparation of durable-press cottons. The two-step radiation process offered the greatest degree of flexibility in predetermining and in selectively controlling the internal deposition of high molecular weight polymer by grafting within cotton fibers in fiber, yarn, or fabric constructions. This process was developed on a pilot scale for the production of graft copolymers of cotton with monomers such as alkyl methacrylates, acrylonitrile, styrene, and vinyl acetate. When the copolymers in fabric form were treated with crosslinking reagents, the cotton fabrics retained higher wash-wear ratings after thirty wash-dry cycles than did products that were only crosslinked.

Research has continued under a P. L. 480 grant at the Cotton Technological Research Laboratory, Bombay, India, to investigate the preparation of radio-resistant and radiosensitive celluloses. When allylated cottons were exposed to cobalt-60 gamma radiation at low dosages (100,000 to 1,000,000 rads), there was an apparent increase in tenacity and other mechanical properties of cotton. These effects were attributed to the presence of double bonds in the allylated samples. Additional work is planned to determine the reaction mechanisms involved. The radiation degradation products of acetylated cellulose were principally acetic acid, cellobiose, and glucose. Preliminary screening of the radiation effects of various chemicals (ethylene diamine, diphenyl amine, ammonia, methanol, isopropanol, butanol, formic acid, acetic acid, glucose, indole, and urea) on cotton was carried out. The amines and alcohols appeared to be radioprotectants for cotton, and indole appeared to be a radiosensitizer for cotton. Based on the reactions of chlorous acid and sodium borohydride with irradiated cotton, it was suggested that radiation-initiated oxidation of cotton occurred primarily at the carbon C-6 position.

3. Mechanisms, Rates and Catalysis of Reactions of Cotton Cellulose and of Chemically Modified Cotton. The kinetics of reactions between cotton cellulose and dimethylolethyleneurea in aqueous and nonaqueous media in the presence of various Lewis acids have been compared with kinetic data obtained under similar reaction conditions wherein dimethylolpropyleneurea and

dimethyloldihydroxyethyleneurea were the etherifying reagents. The metal salt complexes of cyclicpropyleneurea have been compared with the corresponding complexes of cyclicethyleneurea. Effects of magnesium chloride catalyst used in combination with monobasic and dibasic acids on fabric properties of finished cottons have been studied. The fundamental data accumulated in this study should aid in the production of improved durable-press cottons.

It has been found that cottons chemically modified with long-chain monobasic acids in nonaqueous media owe their recovery properties chiefly to increase in percentage of delayed recovery, whereas cottons modified with dibasic acids or acid chlorides under like experimental conditions show improved recovery due to increase in immediate recovery. Changes in crystalline modification of cottons modified with butadienediepoxide from type I to type IV lattice by a postmercerization causes loss in dry wrinkle recovery properties, but subsequent vacuum drying of these postmercerized samples restores the high dry wrinkle recovery. Differential thermal analyses as well as spectral and microscopical analyses are being determined for samples before and after dry recovery is imparted by different modifications. Fine structural analyses of partial esters of a given monobasic acid synthesized by different methods of esterification are being made to elucidate mechanisms of imparting crease recovery to cottons. Such fundamental data are needed to determine effects of bound water and crystalline modification of cotton on recovery and tensile properties of finished fabrics.

4. Soiling of Cotton Textiles. Grant research at the University of Arizona, Tucson, to correlate fiber surface microtopography with soiling of cotton textiles has been completed. In recent work, soil particles consisting of iron or copper were observed adhering to the fibers of a fabric in electron micrographs made with an experimental model of a scanning microscope-electron probe at magnifications of 250X. X-ray pictures made simultaneously show the finely divided iron particles even more clearly, and the chemical nature of the soil is determined by their characteristic X-rays. It is anticipated that further development of this type of instrument will improve the resolution at higher magnifications so that details of cotton fiber rugosities may be observed and lighter elements comprising the soils may be identified *in situ*.

5. Exploratory Physical Investigations of Native and Modified Cotton. Study of physical and chemical properties of yarns and fabrics at stages below and at the recommended level for treating to achieve smooth drying properties in pad-dry-cure, wet-fix, polyset, and easy-cure processes shows that the tensile properties are reasonably consistent with the crosslinks formed during curing. Where yarns and fabrics are treated by the same process, strength losses in yarns are larger than in fabrics. When polymers are allowed to form on fiber surfaces by air-drying in the wet-fix process, fibers can be separated only with difficulty even in low twist yarns. In this, as well as other processes, intrafiber bonds are formed by the treating

process. Efforts are being made to differentiate between the bonds within the fiber and those between fibers in yarns and fabrics and their influence on elastic properties. Properties of fibers and yarns when crosslinks are formed by other processes are being examined.

An investigation of the correlation between several important physical properties of cotton apparel fabrics and their performance in actual service tests has continued in a P. L. 480 project at the Shri Ram Institute for Industrial Research, Delhi, India. Service wear trials on shirts for office personnel and on labor uniforms (shirts and pants) were conducted. A special built-in lubrication finish produced a significant improvement in the wear life of shirts for office personnel. In-service abrasion performance of the shirts correlated best with flex abrasion tests. Shirts worn by labor personnel were subjected to predominantly crosswise stresses. The work pants were subjected primarily to surface abrasion actions and longitudinal pulling. Abrasion performance correlated best with warpwise flex abrasion and retained tensile strengths. Reversing the normally exposed side of 3/1 drill work pants improved abrasion performance, but decreased tear performance. Tear lengths were found to obey an exponential probability law. The results of service wear performance of labor uniforms indicated the existence of occupational bias.

In other P. L. 480 research at the Shri Ram Institute for Industrial Research, relative mass-transfer efficiencies of fluid bed processing, hot air convection and conductive heating for the curing of crosslinking resins on cotton casement fabric were determined. Curing temperatures from 100° to 200°C. were used and the cured fabrics tested for resin fixation, crease recovery angle, and mechanical strength properties. Results confirm previous findings that advantages exist for the fluid bed process as a consequence of its excellent heat transfer characteristics. Use of a finned-tube countercurrent solid-gas contact system increased solids holdup from 8 to 23% of theoretical levels without flooding the column and doubled previously reported heat and mass transfer rates. The studies indicate that the countercurrent method may be practical for commercial use and could demonstrate processing advantages. However, there is no improvement of product quality. Benefit for cotton over that of competitive synthetic fabrics will lie in the reduction of drying costs.

A P. L. 480 project at the Chalmers University of Technology, Gothenburg, Sweden, to investigate the behavior of cotton fibers subjected to aerodynamic forces has been completed. Low-velocity air streams were shown to be ineffective for producing aerodynamic fiber parallelization of cotton fibers suspended in the air stream. However, it was shown that air-suspended fibers could be parallelized in high-speed turbulent air flows in conical channels. The most efficient parallelization occurred in a venturi with a 30° half-angle of convergence, a 2 to 1 ratio of inlet to outlet area, and an air velocity of 30 meters per second or higher.

Some very important basic findings concerning the formations of fiber hooks at the cotton card were developed in a recently completed P. L. 480 project at the Ahmedabad Textile Industry's Research Association in India. The more important of these findings are that the incidence of hooks in the card web is not influenced by the configuration of fibers in the lap, weight of the lap fed, lickerin speed, presence or absence of flats, or method of doffing. It was shown that the pattern of hooking in the card web is affected mainly by cylinder and doffer speeds, sliver weight, and rate of carding. Using a bench model card, it was shown that more than 50% of the majority hooks and 40% of the minority hooks are formed with reversal of fiber ends during transfer from cylinder to doffer. This knowledge permits a more fundamental understanding of the mechanism of fiber hook formation and the possible development of better methods for carding low Micronaire cottons. Because the work was done with an old model card at necessarily low production rates, the conclusion that increased carding rate increases noil removal and decreases yarn strength must be applied with caution with reference to modern, higher capacity cards.

In research under a P. L. 480 grant at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, drafting tenacity measurements in spinning were made on 13 cottons varying widely in fiber length and fineness. These measurements were made in both the normal and reverse drafting directions. Simple correlations were made between drafting tenacity and the 2.5, 50, and 66.7 percent span lengths, and between drafting tenacity and these measurements divided by the Micronaire reading. Correlations were also made between drafting tenacity and various percentages of the Suter-Webb diagram. It was found that drafting tenacity correlated better with the length measurements alone than with the length/Micronaire measurements. The correlations were higher for the normal direction of drafting than for the reverse direction. The coefficient of correlation plotted against percent fiber weight (Suter-Webb diagram, longest to shortest fiber length) decreased for length alone but increased for length/Micronaire.

Research to investigate the effects of atmospheric conditions during the spinning of cotton yarns on yarn properties and spinning efficiency is continuing in a P. L. 480 project at the South India Textile Research Association, Coimbatore, India. Spinning tests on short staple cotton (31/32-inch) have almost been completed and will now be extended to medium and long staple fiber. For the short staple cotton, atmospheric conditions of 70°F. and 41% relative humidity in the spinning room were associated with a minimum number of end breaks during spinning, whereas conditions of 70°F. and 69% relative humidity were associated with maximum yarn (skein) strength.

In P. L. 480 research at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India, effort is being directed toward the development of a stochastic model for determining the efficiency of drafting independent of the size of fibrous strands. In studies of sliver, roving, and yarn, a damped harmonic form of the distribution of the fibers per cross section was

compared with the estimated spectral density of the average number of fibers per cross section obtained with the Uster tester. It was found that the calculated curves were only smoothed out versions of the estimated ones. Attempts were made to obtain the general form of the covariance function, assuming that a damped period is introduced at every drafting stage. It is felt that the covariance function of a strand, in general, can be represented by means of a function that is a mixture of several damped harmonic functions. A general form for the covariance function was devised and found to fit very well for roving but not for sliver and yarn.

Scientists at the Fiber Research Institute, T.N.O., Delft, Holland, have conducted additional P. L. 480 research to obtain information needed to predict the performance of cotton yarns during weaving. The influence of warp yarn tension, different types of yarn imperfections, abrasion resistance, and resistance between the shuttle and the yarn on warp breakage during weaving was investigated. A conventional and small-scale pilot-type loom was used. Warp breaks were not usually caused by weak spots in the yarn or by extremely high tensions. The position of warp breaks was dependent on type of yarn imperfection, and only about half of the total number of breaks was explained by the presence of imperfections in the yarn. Yarn breaks caused by large imperfections resulted from increased abrasion which in turn was caused by high yarn tensions. At normal tensions, warp yarn breaks were not influenced by the yarn coming in contact with the shuttle. Generally, the greatest number of warp breaks are still unclassified as to cause, and it is suspected that loom actions rather than any yarn characteristic are mainly responsible.

A P. L. 480 research study of the factors that affect curling and bursting of preponderantly warp- and filling-faced cotton fabric structures during processing of cotton into end-use products is in progress at the Bombay Textile Research Association, Bombay, India. A number of selvage parameters have been investigated. A great amount of effort was expended in weaving and testing the various selvage constructions employed with twill weaves. Plain weave fabrics are now being woven. Conclusions gathered from the data on twill fabrics give good indications of the best selvage constructions for this type fabric.

C. Technology--Process and Product Development

1. Improved Procedures for Mechanical Processing of Cotton. Intramural research is in progress on the development of optimum textile processing techniques, blends, and products for increasing the utilization of low and high Micronaire reading cottons of medium staple length. A fundamental investigation of the relationships between fiber fineness by length group and yarn strength and end breakage has been conducted on 55 medium staple cottons. It was found that the yarn strength per unit fiber fineness (ratio of yarn strength to fiber fineness) decreases slowly and curvilinearly as fiber length by group increases. Conversely, the ratio of end breakage to fiber fineness increases sharply and curvilinearly as fiber

length by group increases. It appears that the fineness of the longer length fibers is more influential than the fineness of the shorter fibers on yarn strengths and end breakage in spinning.

Complementary research being conducted under contract at Texas Technological College, Lubbock, seeks to provide similar technology to increase the utilization of low and high Micronaire reading cottons of the shorter staple lengths. The contractor had much difficulty in obtaining 144 bales of cotton of the required fiber properties because of the short 1967-68 crop, but processing is now well underway. No definitive findings are available as yet.

In continued research to determine the interaction of processing variables with yarn properties and end breakage, the interrelations among drawing frame processing variables, fiber parallelization, fiber hooks, and processing performance were studied. Fiber parallelization and total fiber hooks decreased with increases in card sliver weight. Parallelization decreased and total fiber hooks increased with increases in first and second drawing sliver weight. Generally, relatively lightweight slivers and better fiber parallelization resulted in more uniform yarns and lower end breakage. Certain draft distributions and back roll weightings improved fiber parallelization and reduced end breakage. For optimum processing performance and improved quality control it is necessary to obtain both fiber parallelization and sliver uniformity measurements. The modified Lindsley technique was adapted so that measurements of fiber orientation can now be obtained with one instrument instead of two.

2. New and Improved Mechanical Processing Machinery--Opening Through Carding. Research on the SRRL Bale-Opener-Blender has been completed. An automatic control system recently developed for the Blender permits continuous unattended operation and enables the machine to produce uniform sized tufts of cotton at production rates up to 1400 pounds per hour. The cotton textile industry now has a suitable means for opening and homogeneously blending up to 20 bales of cotton at high production rates.

Recent research to develop new or improved equipment for feeding cotton to textile carding machines has been limited to the design and construction of modified versions of two experimental devices: the SRRL High Speed Tube Roll and the SRRL Precarder. The Tube Roll, a device that delivers fiber directly to the slower moving surface of the main cylinder of the card, was successfully used on the carding machine: there was no evidence of fiber damage, there were fewer defects and a more uniform distribution of fiber in the card web, and its appearance was improved. The Precarder was modified to produce a web that was more suitable for feeding to a conventional textile card and thus yielded a higher quality cotton product. It is planned to conduct research on a modified conventional card and the Precarder to develop an improved carding apparatus for more efficiently processing higher quality textile products from low-quality cottons.

Two potentially useful techniques have been developed for separating raw cotton into individual fibers to directly feed up to 100 conventional spinning spindles producing yarn. The methods have been thoroughly evaluated and documented for future applications as an initial stage of a fundamentally new system for processing cotton textiles. Limited investigations show that temperature significantly affects cotton fiber friction, as measured by the cohesive resistance of card sliver.

Basic electrostatic experiments with cotton have revealed significant phenomena which suggest potentially practical applications. Cotton tufts with high moisture content tend to open in an electrostatic field. The silent discharge of electrical particles from a single pointed electrode is strong enough to move cotton fibers. Ionically impregnated cotton fibers or yarn will act as a conductor and spin in an electrostatic field. A "tornado effect" or an "electrostatic whirlwind" can be generated between specially shaped electrodes; this result suggests a possible means of forming yarn at high speed. By narrowing the field between two counter-rotating cylindrical electrodes, it is possible to make cotton fibers migrate slowly or rapidly toward the higher field intensity depending on the rotational speed of the electrodes. Several unique ideas are being evaluated for possible incorporation into prototype devices to electrostatically produce a uniform textile strand.

3. Durable-Press Cotton Products. A promising new process--Steam Set--has been devised for the production of improved durable-press cottons. This process, adaptable to pre- or post-cure, is economical and makes efficient use of the polymer former and crosslinking resins employed. It is already evoking considerable industrial interest: some mills are evaluating Steam Set fabrics, and at least one successful mill trial has been run. The new process differs in several ways from the National Cotton Council's wet-fixation process. One difference is that the padded fabrics are steamed, dried, and cured without an intermediate wash step.

The reactivity of crosslinking agents and the ease with which the resultant crosslinks undergo acidic hydrolysis were found to be related: cellulose derivatives from reactive agents were easily hydrolyzed, whereas those from relatively unreactive agents were more difficult to hydrolyze. This very important and useful concept has been justified on practical and theoretical grounds. Varied reactivities for a widely used durable-press agent were shown to be due to impurities in the system and not to the presence of isomers. This general knowledge of reactive systems, effects of catalyst and trace materials, etc., is necessary to achieve optimum finishing of cotton.

Two approaches have proved successful in the laboratory for elimination of the release of free formaldehyde from sensitized cotton fabrics that have been treated with carbamate finishing agents. In one, the solution of agent is modified with a suitable reactant, such as ethyleneurea, which binds the free formaldehyde and prevents its release. In the other, free

formaldehyde is removed from the sensitized fabric by aeration. Development of these methods for application on an industrial scale could make the use of carbamate agents more practical in post-cure durable-press finishing. The mild cure finishing process has been modified and improved to make this method of producing smooth drying cotton more suitable to American plant practice. With the proper combination of crosslinking agent and strong mineral acid catalyst, mild curing conditions yield finished fabrics with high levels of wet and dry wrinkle resistance. These fabrics exhibit good smooth drying properties after laundering and either tumble-, drip-, or line-drying.

Chemical finishing of knit cotton fabrics has not only produced durable-press properties but provided control over other properties such as dimensional stability, stiffness, and hand. This will allow wider use of knit cotton. Durable-press knits should be particularly valuable for apparel because they are more abrasion resistant than conventional durable-press woven cotton. Crosslinking of cotton fabric in superheated steam has given wrinkle resistance and higher strength and abrasion resistance. Apparently, reactions of crosslinking agents are modified by steam. Similar benefits have been obtained from addition of reactive stearamido compounds to formulations for conventional finishing, but this process is restricted to a few crosslinking agents only. The study of active catalysts from substituted organic acids and inorganic salts is leading to a better understanding of these catalysts and catalysts in general. The mixtures are now more adaptable to various finishing procedures. The mixtures form complexes containing an equimolar ratio of acid and salt. An important point in the mechanism is that the organic acid serves as a proton source.

Crosslinked films of polyethylene, polyvinyl chloride, polyacrylates and silicones were formed on coiled cotton yarn. The films imparted durable false twist to the yarn, thus offering a potential means of dimensionally stabilizing knit or woven stretch fabrics. Colored polymer films were formed on cotton fabric by amine dyes reacted with an olefinic tetraepoxide. High durability of the dye-epoxy copolymer films was observed. The bonding efficiency was increased by simultaneous deposition of crosslinked polyethylene as part of the film. This method of dyeing may serve to lessen frosting and fading of dyed durable-press cottons during repeated laundering. In depositing crosslinked silicone films on fabric in conjunction with conventional creaseproofing resin treatments, the use of a softener that catalyzed cellulose crosslinking permitted the concentration of expensive silicone to be lowered to one-tenth its usual level.

The polymerization of acrylamide as a durable, crosslinked film within the fibers of cotton fabric has been studied. Physical changes produced in the cotton were a moderate degree of fiber swelling and an increase in softness. No chemical changes in the cellulose were evident. When N-methylolacrylamide was similarly polymerized in fabric, cellulose crosslinking resulted even in the absence of crosslinking catalyst, particularly if high curing temperatures were used. When N-methylolacrylamide and methyl hydrogen

silicone were applied together to form a crosslinked film of interpolymer in the fabric, high wrinkle resistance was imparted. Benzoyl peroxide was used as the initiator. Certain N-methylol compounds widely assumed to require acid catalysis when used as durable-press agents for cotton have proven effective when used with alkaline catalysts. Methyl hydrogen silicone was bonded to cotton by these agents in the presence of alkaline catalysts.

Durable-press performance has been achieved by use of a wet-fixation system followed by application and heat cure of crosslinking agents and certain reactive additives. Some combinations have yielded durable-press fabrics with 100% strength retention after the scorch test. In addition to reactive polyol additives, some reactive amide additives can be used in producing these scorch-resistant fabrics. Progress in improvement of textile physical properties has been achieved through use of mercerized fabrics, polymer additives, and variations in the chemical reagents and procedures. The attainment of scorch-resistant fabrics is an important requirement to permit the application of a fixation finishing system to white goods. Durable-press performance has also been achieved by using urea and formaldehyde in a wet-fixation system. Grafting reactions employing polyol additives in a pad-dry-cure system were used to produce fabrics with either improved breaking strength or soil release properties.

Various polymer formulations were applied as sizing to commercial denim yarns. Fabrics woven from these sized yarns were successfully dyed and finished by conventional methods. Significant improvements in durable-press fabric properties and abrasion resistance resulted from polymer-treating the yarns. High wash-wear and crease ratings were obtained by using much lower resin concentrations than employed in conventional treatments. Polymer sizes produced yarns with good weaving efficiency at low relative humidities.

The contractor (Fabric Research Laboratories, Dedham, Massachusetts) has completed the testing of physical properties of various 5.4 and 8.1 ounce fabrics made from 50/50 blends of untreated and resin-treated cotton fibers. Planar shrinkage of the fabrics and shrinkage and home laundry abrasion resistance of trouser cuff specimens have been determined. Selected fabrics that exhibited the best combination of resistance to abrasion, smooth drying characteristics, and crease retention will be subjected to mechanical shrinkage to improve their dimensional stability.

Sixteen N-methylol cellulose reactants were compared on broadcloth and sheeting in the one-step Polyset Process using mixed zinc salts as catalyst. None of the reactants showed exceptional promise for durable-press fabrics. Even when the fabrics had acceptable smooth dry appearance, their physical properties were not significantly superior to those obtained by conventional pad-dry-cure treatments. However, all of the treated fabrics were resistant to yellowing on subsequent washing with chlorine bleach. In another study, room temperature wet curing of broadcloth and sheeting with

a trimethylolmelamine resin and zinc acetate catalyst resulted in high retention of strength but low wrinkle recovery in comparison with untreated control fabric. A second treatment with a latent acid catalyst greatly improved wrinkle recovery, and subsequent tests showed only a slight reduction in abrasion resistance and tensile strength. Curing with superheated steam as the first step had about the same effect as wet curing.

Yarn mercerization has proven extremely effective in preventing strength losses during subsequent wrinkleproofing of fabric woven from the yarn. High strength retention was obtained previously at medium or "wash-wear" levels of wrinkleproofing, but now has been demonstrated at much higher, or "durable-press," levels. Slack mercerization followed by restretching in mercerizing alkali was the optimum yarn treatment; however, even mercerization at constant length served to double the fabric strength retained after durable-press treatment. Commercial mercerization of yarn proved extremely effective in fortifying knit fabric against strength losses during durable-press treatment of the fabric. In knit fabric, the strength retention was somewhat dependent on the wrinkleproofing agent chosen but not on concentration of agent, whereas in woven fabric the choice of agent had almost no effect but concentration had a significant effect. Knit fabrics offer unusual opportunities for durable-press treatments at higher resin levels than are practicable in woven fabrics.

Chemically blocking the most accessible hydroxyl groups on the cellulose molecule by partial acetylation before crosslinking improved the wet wrinkle recovery, flex and flat abrasion resistance, and breaking and tearing strength of durable-press fabrics. Research is now in progress to develop a simple low level cyanoethylation treatment, which theoretically should achieve the same results, and to evaluate the effect of this treatment upon subsequent crosslinking and outdoor weathering treatments. Numerous screening treatments indicated that padding the fabric in a 5% sodium hydroxide solution followed by treatment with 100% acrylonitrile in a cylinder gave the best results. In other work, methods were developed for the stabilization of greige or desized fabric to the formation of longitudinal wrinkles during rope bleaching. By low level crosslinking of the fabric prior to rope bleaching, it was found possible to greatly reduce wrinkle formation and improve the appearance of the finished fabric.

Further contract research has been conducted by Auburn Research Foundation, Inc., Auburn, Alabama, to develop mechanical-chemical surface treatments to improve the abrasion resistance of durably pressed cottons. Mechanical treatments of cotton fabric, both stretching and compressive shrinkage, were investigated in combination with treatments such as crosslinking and the use of polyurethane to impart smooth drying characteristics. The most promising treatment is one in which fabric is impregnated with a polyurethane film former and a small amount of crosslinking agent, dried and compressively shrunk, stabilized by curing, and, finally, crosslinked more

extensively. This treatment has given good strength and abrasion resistance, but further research is needed to obtain better than marginal smooth drying properties.

Research was initiated in cooperation with the Cotton Producers Institute to further elucidate the role of fabric structure in the durable-press performance of treated cotton fabrics. A statistically designed experiment requiring the preparation and evaluation of 400 experimental fabric structures has been planned. Eight bales of cotton from a standard mill mix are on hand, and preparation of the experimental fabrics will begin soon.

Another cooperative study with the Cotton Producers Institute is aimed at developing improved cotton fabrics for durable-press work trousers. In initial experiments, a series of chemical treatments for imparting durable-press properties was applied to a standard twill control fabric, and the fabrics were evaluated for home laundering wear, appearance, and other physical properties. In general, the fabrics exhibited good smooth drying properties. Fabric treated by an experimental wet-fixation durable-press process wore best. Additional experimental fabrics are being prepared for evaluation.

A vapor phase technique for crosslinking cotton with formaldehyde was investigated. Applicable to existing garment curing ovens, the system utilizes a thin walled, expandable container that encloses the cotton garments and the liquid reagents which are spread in a thin layer on a matrix having a large surface area. Good results were obtained with cotton print cloth when the containers were made of polyethylene film and the liquid reagent of formalin-sulfur dioxide was dispersed on glass fabric. Optimum process variables have not been established. Commercially the technique would offer simplified, accurate control with minimum investment to manufacturers of durable-press garments. It also offers a laboratory procedure for studying other vapor phase reactions. The formalin-sulfur dioxide liquid reagent used in vapor phase has also been found to be an efficient crosslinking system in conventional pad-dry treatments. Impregnation and drying achieve reaction without the need for high temperature curing.

4. Weather-Resistant Cotton Fabrics. Cooperative work with the Canvas Products Association International and the Cotton Producers Institute has resulted in the development of several promising treatments for outdoor cotton fabrics. The inclusion of paraffin wax-ammonium stearate emulsion with a Zirchrome fungicidal mineral dye bath to produce a single-bath process for fungicidal mineral dyeing and water-repellent finishing was successfully accomplished on a laboratory scale. A modification of the process is being developed to eliminate byproduct hydrophilic alkali salts in the treated fabrics to enhance the Paraffin-Zirchrome water repellency. A process for depositing orange to brown fungicidal mineral dyeings from a single bath was also discovered. Two companies have licensed patents, and five companies are engaged in coordinated development work for commercial use of the research developments. Research studies are underway to combine

phenyl mercury-zirconium finishes in durable-press treatments in order to obtain durable biocidal properties. New single-bath mineral dye, fungicide, and water-repellent systems are being developed to reduce conventional processing steps and chemical controls and to obtain attractive color shades and improved weatherability.

Comparative studies (soil burial and water leaching) of cotton duck samples treated with copper borate-zirconium ammonium carbonate or copper borate-zinc ammonium carbonate indicated that the combined microbial resistance of copper and zinc increased the resistance of these treated samples to rotting. Seed bed cover fabric treated with zinc salt catalyzed methylolmelamine resin and titanium dioxide (rutile) pigment has been prepared on commercial equipment and is under test. A number of samples of duck have been treated with iron, chromium, cobalt, cadmium, and manganese; these are being tested in soil burial and for resistance to water leaching. Samples of duck treated with potential air pollution degradation inhibitors have been laboratory-tested and the results indicated that zinc oxide and zirconium oxide may be useful.

The cooperative research has shown that cotton osnaburg treated with N-methylolmelamine resin has good rot and weather resistance. Prior weathering somewhat reduced its resistance to subsequent rotting. Sandbags made from resin-treated osnaburg meet military specifications; however, tearing strength is marginal and its improvement would make the sandbags more attractive to the military. The use of softeners in this finish failed to improve tear strength. Wet curing of the resin resulted in greatly improved tensile properties with no loss in rot and weather resistance. Tests on all-cotton duck and cotton-rayon blend duck indicated that the blend was not as superior as claimed. Samples treated with zirconium-copper and selected mixed pigments showed excellent strength retention after 24 months of exposure. Arrangements were made with the state of New York for a series of air pollution-fabric degradation studies at a number of sites in New York State. Statistical analysis of compass octant exposures of cotton fabric revealed that no significant acceleration of degradation could be achieved by re-orienting the exposure racks.

Contract research to develop improved coated cotton fabrics with optimum strength-weight characteristics for outdoor uses has continued at Fabric Research Laboratories, Inc., Dedham, Massachusetts. Two techniques were found for minimizing the loss in tearing strength that results when a woven cotton fabric is coated. One technique is to use a soft base coat, covered by a harder surface coat if necessary. The other is to use a water-soluble material to fill the pores of the fabric prior to coating, then coat and cure, and finally remove the water-soluble material by washing. The first technique is especially useful in that it makes it possible to take advantage of the high initial tearing strength provided by twill or basket weaves.

5. Soil-Resistant Cotton Textiles. An experimental finish for cotton fabric based on a fluorinated urea gave high oil repellency and moderate water repellency, both of which were more durable to home laundering than similar properties imparted by the newer commercial stain-release finishes based on fluorocarbons. Chlorine damage on fabrics treated with this finish was lower than with a commercial fluorocarbon finish. The fluorourea finish was incompatible with a widely used permanent-press reagent in applications from aqueous dispersions. Attempts to prepare derivatives of this urea with better compatibility with aqueous systems have thus far been unsuccessful. During a study of the chemistry of the fluorourea finish, a fluorinated methylolurea was isolated; such a derivative should be useful in obtaining oil and water repellency.

Another experimental finish, based on a fluoroamine and THPC, was not as durable as the fluorourea finish. A high-temperature cure after the usual ammonia cure in the application of the fluoroamine-THPC finish to cotton fabric slightly increased the durability of the finish to laundering and solvent extraction. In comparison with other fluorochemical finishes, this finish showed good soil release and low soil redeposition.

6. Insect-Resistant Cotton Bags. Research to develop improved insect-resistant cotton bags for the storage and shipment of milled cereals was continued in cooperation with the Stored-Product Insects Research and Development Laboratory at Savannah, Georgia, the Textile Bag Manufacturers Association, and the Agricultural Stabilization and Conservation Service. The laboratory accelerated storage test devised to evaluate insect-repellent formulations for insect-resistant treated bags was found to correlate with large-scale storage tests. This permits quicker screening of experimental formulations. Incorporation of materials such as castor oil, vegetable oils, long chain fatty acid derivatives, hydroxy compounds, and polymeric latex emulsions in the formulations appeared effective in inhibiting loss of insect repellent from the treated fabrics. Use of polyvinyl chloride films as barriers between the treated fabrics and the stored foods retarded the migration of insect repellent into the foods. In an overseas test-shipment of cornmeal to the Philippines, insect-resistant treated cotton-paper laminated bags and insect-resistant treated paper bags showed adequate insect resistance but inadequate protection from physical damage. Now awaiting evaluation are proposals for modifying the construction of the cotton bags to eliminate seams and damage at the corners and for using film inserts in the treated cotton bags to act as barriers.

RPA 705 - SELECTION AND CARE OF CLOTHING AND HOUSEHOLD TEXTILES

A. Chemical and Physical Investigations to Improve Products

1. Better Fitting Consumer Apparel. Contract research is in progress at Boston University, Boston, Massachusetts, to obtain data on body dimensions needed in the development of satisfactory systems for sizing apparel for

elderly women. Because the currently used sizing systems are inadequate, many older women must make or pay for extensive alterations in order to obtain well-fitting clothing. The contractor has obtained a considerable number of measurements of importance in sizing such apparel, and is tabulating and analyzing the data.

RPA 709 - REDUCTION IN HEALTH HAZARDS INVOLVED IN USE OF NONFOOD FARM PRODUCTS

A. Chemical and Physical Investigations to Improve Products

1. Prevention of Microbiological Contamination of Textiles During Laundering. In contract research at Southern Research Institute, Birmingham, Alabama, experiments designed to determine to what extent vaccinia virus survives and is transferred to other fabrics during laundering of virus-contaminated fabrics in cold (70-80° F), warm (100-110° F) and hot (130-140° F) water have been completed. Experiments on the transfer of vaccinia virus during the dry tumbling of inoculated with uninoculated fabrics have also been completed. Similar experiments on the dissemination of poliovirus during the laundering and dry handling of virus-contaminated fabrics are in progress.

B. Technology--Process and Product Development

1. Flame-Retardant Cotton Textiles with Other Desirable Properties. Cotton fabrics treated with solutions containing tetrakis(hydroxymethyl)-phosphonium hydroxide (THPOH) and trimethylolmelamine in various molar ratios and processed by a pad-dry-ammonia cure followed by a high-temperature heat cure were rendered durably flame resistant. Substitution of the less expensive trimethylolmelamine for a portion of the more expensive THPOH has resulted in reduction in cost of the THPOH-ammonia flame-retardant treatment. Fabrics treated by this process had good strength properties as well as good hand. Trimethylolmelamine was more effective in this treatment than numerous other reactive nitrogen compounds evaluated.

Cotton fabrics impregnated with the THPOH flame retardant were also made flame resistant by use of anhydrous ammonia gas as both the drying and curing agent. The successful development of this technique eliminated the heat-drying step prior to ammonia curing and simplified the process. Application of THPOH by this process was more effective when conducted at ambient temperature. Application of THPOH and of other flame retardants based on THPC and THPOH by this process followed by exposure to dry steam was less effective. Little or no strength losses were observed in THPOH-treated fabrics processed by the ammonia dry-and-cure technique.

The addition of copper salts to THPOH stabilized the solution to polymerization with ammonia, thereby making it possible to apply THPOH to cotton in the presence of aqueous ammonia by a pad-dry-cure procedure. This method

not only improved the flame retardancy of cotton but also improved the rot resistance due to the presence of copper. Good flame retardancy, stable to 30 home launderings, was obtained on cotton fabric by incorporating trimethylolmelamine in an ammonium hydroxide solution of THPOH stabilized with cupric nitrate. By this technique of increasing the nitrogen content, less phosphorus was required for flame retardancy.

Industrial interest in several of these finishes has continued to increase because of the excellent properties exhibited by the treated fabrics.

The DAPT finish, a new flame retardant based on the formaldehyde derivative of a triazine phosphonate, was also developed. This retardant is chemically similar to methylolmelamine except that it contains phosphorus, an element necessary for durable flame retardancy. It polymerized readily on cotton without a catalyst when heat cured. When this new finish was applied to cotton sateen with a softener, the treated fabric had good flame retardancy, strength retention, abrasion resistance, and no discoloration.

In cooperation with the U. S. Army Natick Laboratories, Natick, Massachusetts, research to impart flame and rot resistance to cotton is being conducted. Sateen and print cloth treated with a solution containing a 1:2 mole ratio of THPC:cyanamide and 2% phosphoric acid passed the standard vertical flame test after 30 launderings. The phosphorus content remained essentially unchanged after laundering. This treatment was also successfully applied to cotton on a pilot plant scale. A method was found for incorporating organolead compounds such as thioethyltriphenyllead in a THPOH-ammonia flame-retardant system. Cotton print cloth treated with an emulsion containing 5% of the organolead compound retained 55% of its breaking strength after 12 weeks of soil burial. Cotton print cloth treated with thiobutyltriphenyllead solution to contain 0.80% lead retained 100% of its breaking strength after 8 weeks of soil burial.

2. Flame-Retardant Cotton Batting. Research to develop efficient low-cost flame-retardant treatments for cotton batting was continued in cooperation with the National Cotton Batting Institute, the Textile Fibers and Byproducts Association, the National Cottonseed Products Association, the Foundation for Cotton Research and Education, and the National Association of Bedding Manufacturers. Cotton linters and textile wastes were impregnated with low-cost semidurable flame retardants and then the treated fibers were mechanically processed into cotton batting products. Inclusion of nitrogen-containing resins in the formulations used for pretreatment enhanced the fibers' resistance to burning. Such processing also improved the resilience of the products. Some increase in fiber breakage during garnetting seems to be an inherent result of pretreatment; however, there are indications that this damage can be minimized by including a softener in the treating formulation. Representatives of the chemical and batting industries, equipment manufacturers, and government are intensely interested in this research in anticipation of the implementation of the Flammable Textiles Act Amendments of 1967 and of the Highway Safety Act of 1967.

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RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL PRODUCTS FROM FIELD CROPS

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AREA 2 - COTTONSEED UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
406	New and improved food products from field crops			
	Chemical composition and physical properties	3.0		3.0
	Technology--process and product development	8.6		8.6
	Subtotal	11.6		11.6
407	New and improved feed, textile, and industrial products from field crops			
	Chemical composition and physical properties	7.2	0.3	7.5
	Microbiology and toxicology		0.8	0.8
	Technology--process and product development	1.2		1.2
	Subtotal	8.4	1.1	9.5
702	Protect food supplies from harmful microorganisms and naturally occurring toxins			
	Microbiology and toxicology	8.5	1.8	10.3
	Subtotal	8.5	1.8	10.3
	TOTAL	28.5	2.9	31.4

Domestic program supplemented by P.L. 480 funds in 4 countries totaling 70,339 U.S. dollars equivalent per year (India, Israel, Japan, and Italy).

Problems and Objectives

Cottonseed products face increasing competition for markets: edible products from the oil must compete with those from other vegetable oils and animal fats, and the meal--now used chiefly as a protein supplement in feeds for ruminants--is being supplanted by synthetic urea and other sources of nitrogen. To retain these markets and to open new ones is the goal of utilization research on cottonseed. Food products must be developed to improve the competitive position of cottonseed oil and meal, to provide inexpensive protein concentrates for domestic low-income groups, and to help alleviate the worldwide protein shortage. There is also need to improve the quality and nutritive value of meal used for feeds. However, the wholesomeness of both food and feed products must be assured by controlling various undesirable natural or adventitious components. Finally, to extend cottonseed's markets beyond food and feed, research is needed to derive industrially useful products.

Specific objectives of the research are:

1. To improve processing methods to preserve or enhance the intrinsic desirable qualities of the oil and meal.

2. To develop new and improved food, feed, and industrial products.

3. To expand domestic and foreign markets for cottonseed products by tailoring them to meet consumer preferences.

4. To insure the safety and wholesomeness of cottonseed products used for food or feed.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Properties of the Triglycerides. Scientists at the University of Bombay in India are conducting P. L. 480 research to determine the properties of pure saturated di- and triacid triglycerides of cottonseed oil. Numerous intermediate compounds were first prepared, including pure fatty acids, methyl esters, fatty acid chlorides, fatty acid anhydrides, 1-monoglycerides, and 1,3-diglycerides. These intermediates were then used to prepare 33 triglycerides by three procedures. Purity was determined by thin-layer and gas chromatography.

2. Structure and Properties of the Proteins. In P. L. 480 research at Kyoto University, Japan, the chemical composition and reactivity of the nucleic acids present in cottonseed are being investigated. Fifteen nucleic

acid components were isolated from cottonseed and identified. Their presence in cottonseed is significant in the physiology of the seed and in the use of nitrogen analysis as a measure of the protein content, as commonly employed. Purified transfer ribonucleic acid (tRNA) material from cottonseed was characterized in terms of sedimentation constant ($3.8S_{20}$), thermal denaturation profile (partially base paired structure formed), base and phosphorus composition (similar to wheat tRNA), and amino acid acceptor activity (greatly reduced by polar defatting solvents).

Under a P. L. 480 project at the Hadassah Medical School of the Hebrew University in Jerusalem, Israel, cottonseed proteins were used as model substrates in a study of improved methods of hydrolysis to cleave proteins without the destruction of amino acids that occurs in conventional procedures. The hydrolysis closest to completion was obtained with enzymes isolated from species of Trypanosomidae. The research has yielded a modified concept of protein nutrition in higher animals and of the probable importance of certain peptides in protein metabolism.

Protein concentrates were prepared from defatted meals by air classification in commercial pilot-plant equipment. This process should provide two high protein quality products--one for food, one for feed--at less cost than wet operations. With glandless seed, the basic process is independent of seed variety and quality and type of equipment. An alkaline wash procedure increased the nitrogen content of Isolate-I to meet the definition of more than 90% protein. The acid solubility of the major protein isolate, Isolate-II, an important property for use in protein-fortified beverages such as citrus drinks, is due to dissociation of the protein to low molecular weight units. Isolates-I and -II differ in isoelectric point, molecular weight, and amino acid composition--all important determinants of functionality. The major protein in cottonseed is extremely low in sulfur amino acids. Glandless flour, concentrate, and isolate were used to produce bread (sponge and dough formulation) comparable to that containing nonfat dry milk (3%). Isolate-II gave excellent bread at the 15% level. Glandless meals made in equipment simulating commercial operations were equivalent in air classification and extraction characteristics to meal processed at room temperature. This research was partially supported by the National Cottonseed Products Association and the Foundation for Cotton Research and Education.

B. Technology--Process and Product Development

1. New and Improved Products from the Oil. A number of procedures for preparing sucrose esters were devised and tested. One procedure gave good yields under conditions that could be employed in large-scale manufacture. It consists of heating molten sucrose for about ten minutes with fatty acid esters of high-boiling alcohols such as diethylene glycol monomethyl ether or glycerol in the presence of alkali metal soaps, which function as catalysts and solubilizers of the immiscible reactants. The chief advantage over current commercial processes lies in the elimination of the expensive

and toxic solvents needed to solubilize the sucrose. These solvents leave toxic residues that have barred commercially produced esters from food use. Food grade sucrose esters have excellent commercial potential. The improved methods of analysis developed revealed that the compositions of sucrose esters produced by interesterification are quite different from those previously reported.

Based on leads developed in the research described above, now terminated, more economical processes are being devised for the production of sugar and other polyol esters of cottonseed fatty acids. The ability of different soaps to function as catalyst-solubilizers in the interesterification of sucrose and fatty acid esters at high temperatures varied markedly. Soaps of oleic acid were superior to those of palmitic acid, whereas those of the short-chain fatty acids performed poorly. Potassium soaps were slightly better than sodium soaps, which formed the firmer emulsions at elevated temperatures. Lithium soaps of unsaturated fatty acids were the most active, but the sucrose esters produced were always highly acylated. Mixtures of potassium and lithium oleates are the preferred catalyst-solubilizers among those tested so far. Monoglyceride products prepared from hydrogenated and unhydrogenated cottonseed oils and containing only 28% monoglycerides could be readily interesterified with sucrose during seven minutes at 185° C to yield surface active products containing monoesters of both sucrose and glycerol. After simple purification, such products should have potential as low-cost emulsifiers for food use.

Confectionery fats made from cottonseed stearine contain appreciable amounts of 2-oleodipalmitin (POP) and 2-elaidodipalmitin (PEP). These two compounds were examined to determine their physical properties. Five polymorphs of POP and four of PEP were found by dilatometric methods, then confirmed by X-ray. Rates of change from one form to another varied from slow to very rapid. These differences in behavior help to explain the properties of confectionery fats containing these compounds. Slow cooling of a partially melted mixture of POP and PEP promoted segregation of the components which, on heating, had melted more or less independently of each other. Cottonseed oil subjected to two fractional crystallizations yielded a 6% fraction melting at 22-29° C and consisting of 20% POP and 80% 2-linoleodipalmitin. This fraction could be used as a low melting confectionery fat.

Laboratory procedures have been developed for the preparation of a new, nylon-base hydrogenation catalyst for vegetable oils. Nylon was precipitated from a solution in such a manner that the particle size was 7-20 microns. This precipitate was treated with platinum or palladium compounds to produce submicroscopic deposits of metal, presumably at the sites of amide groups. Experimental hydrogenations conducted with these catalysts revealed that some could be used under conditions that produced relatively small proportions of trans isomers--the objective of the research. Possibly some of these catalysts will be useful in producing new and improved fat products

from the stearine fraction of cottonseed oil obtained in commercial winterization. At the very least, novel hydrogenation catalysts for fats and oils have been developed.

2. Other Edible Products. Processing conditions were established and used for the preparation and extraction of pilot-plant quantities of glandless cottonseed, meals, and flours having desirable qualities of light color, high protein content, and high protein solubility. The conditions were verified in a test run of 2,000 pounds of cottonseed flakes in a continuous pilot plant in an industrial firm. Conditions were comparable to those used commercially. In a subsequent extraction at the same company, 2,100 pounds of essentially hull-free meal were produced from 10,000 pounds of glandless seed. This meal will be used for future protein isolate studies. Two 5,000 pound lots of seed were processed at SU to produce 2,700 pounds of meal for preparation of protein isolates in another company's pilot plant. Microbiological analyses of samples showed a wide range in total plate counts, low yeast and mold counts, variable amounts of coliform, and occasionally confirmed E. coli. Nutritional evaluation of meals produced before this reporting period showed that glandless meal was superior to glanded meal when fed to rats. Results of chick feeding tests, though inconsistent, indicated that glandless meal is safe to use as a chick feed. Information derived in this terminated research will now be used to modify processes for yielding edible products from glandless cottonseed.

Edible flour from undefatted and defatted glanded cottonseed has been produced by continuous operation of the liquid cyclone process pilot plant. The flour, which is light yellow and bland, contains from 65 to 70% protein, about 3.9 grams EAF lysine per 16 grams nitrogen, 0.11 to 0.30% total gossypol, less than 0.05% free gossypol, and a nitrogen solubility greater than 96%. Thus, for the first time, high quality, edible grade flour has been produced from glanded cottonseed by a continuous process. A procedure developed appears suitable for detecting and measuring as little as 5 ppm of residual hexane and acetone in meals and flours. This development stemmed from the need for a sensitive method for determining trace amounts of these solvents in products destined for food.

RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Improved Cottonseed Meal for Feeding to Nonruminants. Research is continuing on the isolation of cottonseed protein by mechanically isolating intact aleurone grains. The gossypol-rich fraction of cottonseed, prepared with the liquid cyclone and observed with the scanning electron microscope, was found to be composed mostly of whole gossypol glands. The two protein-rich fractions contained aleurone grains (subcellular sites of protein storage) and structureless fines. Both protein-rich fractions were similar

in content of these components. Size distributions of gossypol glands and aleurone grains were determined to provide the data for efficient operation of the liquid cyclone process. Extraction of lipid from cottonseed tissue with nonaqueous solvents had no effect on intracellular ultrastructure other than loss of lipid from spherosomes (subcellular sites of lipid storage). However, mixtures of nonaqueous solvents saturated with water (3% water or less) disrupted spherosomal membranes and extracted a nonlipid that contains phosphorus.

In recently initiated analyses of cottonseed for optically active gossypol and other potential toxins, gossypol was isolated as dianilinogossypol from an aged and from a fresh sample of cottonseed. The derivative from the aged seed had 2-3% activity (+) and that from the fresh seed 21% (-). This first report of the existence of optically active gossypol in cottonseed could reconcile contradictory statements in the literature concerning the toxicity of gossypol and its ability to form certain isomeric derivatives.

The reaction products of gossypol with esters and triglycerides are being studied in contract research at Savannah State College in Georgia. Interesterification of gossypol with methyl stearate formed an amorphous, alkali-insoluble product that seemed to be polymeric. Infrared spectra suggested the presence of bonded or hindered gossypol carbonyl groups; ester bonds between gossypol and stearic acid; and long chain groups, probably stearic acid, in the product.

Spectroscopic properties, including electronic and vibrational absorption, were determined for a number of important metal-gossypol complexes of Co^{++}, Ni^{++}, and Cu^{++} and compared with those of 2-hydroxy-1-naphthaldehyde. The infrared data on 2-hydroxy-1-naphthaldehyde-anthranilic acid indicates that carbonyl groups are involved in a salt-type linkage (dimer) with copper atoms. Electronic absorption spectra of several Schiff base complexes of 2-hydroxy-1-naphthaldehyde were also investigated. These results, in conjunction with the magnetic susceptibility data, were evaluated to arrive at conclusions about the structure of gossypol complexes. After the properties of the various complexes are understood, a specific complex can be selected for use in the inactivation of gossypol. Its effectiveness will then be evaluated by animal feeding tests.

Acetone-hexane-water azeotrope extracts of hexane-defatted cottonseed meal were investigated. Free fatty aldehydes that occur in cottonseed may destroy lysine and reduce the nutritive quality of the protein. Phosphatidyl-inositol, -serine, and -ethanolamine, lecithin, lysolecithin, and two unidentified phospholipids were isolated. A micro-method based on silver nitrate oxidation was developed for analysis of phospholipids. The data showed that G. hirsutum and barbadense (Pima) are products of a hybridization of an ancestral herbaceum and one of the genome D group, with a subsequent doubling of chromosomes. Glandless, but not glanded, cottonseed contains a high concentration of glucosamine. A fatty acid, equivalent chain

length 19.6, occurs in the phospholipids but not in the oil of hirsutum and in high concentrations in seed oil of anomalum (the kernels of which contain 75% oil). Seed from species of Gossypium belonging to genome C contain very little gossypol. The data obtained should be of value to geneticists in developing new cotton species of commercial value and to processors in improving cottonseed products.

In a P. L. 480 project at the University of Madras, India, the properties of the solvent system hexane-acetone-water are being investigated to obtain fundamental information needed in the design of solvent recovery systems to be used in an improved mixed solvent process for conversion of cottonseed to oil and meal.

2. Derivatives of Fatty Acids Potentially Useful to Industry. Preliminary research is being conducted to determine the structure and properties of cottonseed fatty acid derivatives from spectral data. Fundamental information derived will be useful in developing newer methods of analysis and new and potentially useful products from cottonseed fatty acids.

At the Indian Institute of Science, Bangalore, India, a study of the addition of carbenes to unsaturated fatty acid derivatives of cottonseed oil has now been completed under a P. L. 480 project. The addition of dichlorocarbene, dibromocarbene, and carboethoxycarbene to the olefinic moiety of methyl oleate, mixed methyl esters of cottonseed oil, and the oil itself was investigated. The addition of dichlorocarbene at the olefinic linkage of these materials did occur, but the reaction was not complete. The product was characterized by chlorine analysis and infrared examination following purification by column chromatography. Attempts to cause addition of dibromocarbene were not successful. Addition of carboethoxycarbene to methyl oleate yielded cis and trans isomers, which were isolated and characterized. Preliminary screening of the carboethoxycarbene adducts indicated that they may have some degree of antibacterial activity. Since these adducts are bifunctional or polyfunctional, they have potential for industrial application.

Also completed is a P. L. 480 project at the Israel Institute of Technology, Haifa, Israel. The reaction of iron carbonyl with polyunsaturates was studied by use of simple conjugated dienes and trienes as model compounds. The study was then extended to the more complicated systems of betaionone and vitamin A. Iron tricarbonyl pi-complexes of terpenes such as myrcene and levopimaric acids were prepared. Ferric iron was found to isomerize levopimarate to the abietate. Iron tricarbonyl complexes of methyl eleostearate formed two types of complexes: one retained a free olefinic bond conjugated with the complexed diene system; in the other, the free olefinic linkage migrated out of conjugation.

Other P. L. 480 research at the Hebrew University of Jerusalem, Israel, is directed toward modifying unsaturated cottonseed fatty acids by metalation reactions. A qualitative thin-layer chromatographic method and a

quantitative mass spectrophotometric method were developed for determining the position of carboxyl groups in reaction products from metalation reactions. Also studied was the metalation of a stearolyl alcohol and the related methyl ether and of a series of isomeric compounds each of which has a triple bond in one of the successive positions 5 through 11. Dimetalation of monometalated compounds proceeded more rapidly than did the initial metalation: the second metal was attached to the metalated carbon, the reaction products were mixtures of allenes and alkynes with allenes predominating, and the terminal functional group of the compounds having a 5,6-triple bond exerted a marked directional effect on the reaction. Study of the metalation of linoleyl alcohol and the related methyl ether was continued. Carbonation occurred at the 13, 9, and 11 positions in decreasing order of frequency. The mechanisms involved in the formation of the various reaction products have been explored.

At the Indian Institute of Science, Bangalore, India, scientists are studying the chemical transformation of saturated fatty derivatives from cottonseed oil under a P. L. 480 grant. Tertiary α,β-olefinic compounds (1,1-diphenyl-1-butene, 1,1-diphenyl-1-hexadecene, and 1,1-diphenyl-1-octadecene) were prepared by the Grignard reaction of phenyl magnesium bromide with the ethyl esters of butyric, palmitic, and stearic acids, respectively. Hydroboration followed by oxidation and hydrolysis of 1,1-diphenyl-1-butene produced a mixture of 1,1-diphenyl-1-butanol and 1,1-diphenyl-2-butanol and unreacted 1,1-diphenyl-1-butene. The organoborane derived from 1,1-diphenyl-1-butene was isomerized by heating between 190° and 195° C in bis(2-methoxyethyl) ether for three hours. The product was oxidized with alkaline hydrogen peroxide to yield a mixture of 1,1-diphenyl-1-butanol, 1,1-diphenyl-2-butanol, 4,4-diphenyl-2-butanol, and 4,4-diphenyl-1-butanol. These products were identified by comparison with authentic samples on a thin-layer chromatographic plate. The separation of the products by vapor phase chromatography is in progress.

New chemicals were derived from acrylonitrile and fatty acids of cottonseed and other oils as a result of P. L. 480 research conducted at the Hebrew University of Jerusalem, Israel. Some of the reaction products may have potential as plasticizers or rubber softeners.

The synthesis and properties of newer-type glycol monoalkyl ethers based on cottonseed oil fatty acids are being investigated under a P. L. 480 project at the National Chemical Laboratory, Poona, India, to determine their usefulness in suppressing water evaporation from the surface of storage areas. The alkoxy propanols and butanols of the C_{16}, C_{18}, and C_{22} saturated n-alcohols were prepared to complete the series of compounds envisaged in the research plan. In retarding evaporation from large containers placed outdoors and from petri dishes in a wind tunnel, the n-alkoxy propanols and butanols did not perform as well as the corresponding n-alkoxy ethanols. However, for a given hydrophilic group, such as the ethanol, the ability to retard evaporation increased as the chain length of the alkoxy group increased. Equilibrium spreading pressure, collapse pressure, and

pressure-area isotherms obtained for the saturated straight-chain C_{17} and C_{19} alcohols were compared with those of similar alcohols of even carbon number. Dipole moments were calculated from dielectric constants, densities, and refractive indices. Various other thermodynamic properties of the n-alkoxy propanols and butanols were measured or calculated, including surface tension, latent heat of surface formation, and entropy and enthalpy of surface formation.

B. Microbiology and Toxicology

1. Effects of Gossypol in Feed. The digestion and metabolism of gossypol in cottonseed meal are being studied in contract research conducted by the Texas Agricultural Experiment Station at College Station. Balance studies of the metabolic fate of ^{14}C-formyl labeled gossypol in rats and laying hens indicated that gossypol is poorly absorbed from the gastrointestinal tract and is rapidly eliminated from the animal body. In the rat, supplementing the diet with ferrous sulfate enhanced elimination. The ferrous sulfate may form insoluble iron gossypol compounds and may also catalyze the decarbonylation of gossypol. The accumulation of dietary gossypol in the tissue of rats was highest in the liver, kidney, spleen, and heart. In the laying hen, gossypol was rapidly excreted through the combined feces and urine. The concentration of gossypol in the bile was higher than in tissues. This result indicates that the bile is a major pathway by which absorbed gossypol leaves the body and that decarbonylation is not a major route in the laying hen. A major portion of the absorbed gossypol was concentrated in the eggs, and only a small proportion was deposited in the tissues.

Related research is being conducted at the "Mario Negri" Pharmacological Institute, Milan, Italy, in a P. L. 480 project originally designed to determine the mechanism by which L-lysine counteracts the toxicity of gossypol fed to susceptible animals. However, since early findings indicated that L-lysine did not protect against gossypol, attention was focused on other inactivating systems, which are now being investigated.

C. Technology--Process and Product Development

1. New Products Suitable for Industrial Use. Approximately 40 additional N-substituted fatty acid amides were prepared and characterized. These compounds and many others on hand from earlier work were extensively screened to correlate molecular structure with a variety of useful properties. Properties investigated included not only activity as antimicrobial agents, fungicides, nematocides, herbicides, disbudding agents, and antimalarials, but also use as fabric softeners, conditioners for permanent press fabrics, stabilizer-plasticizers for vinyl asbestos tile, and plasticizers for polyvinyl chloride. One of these compounds is being evaluated commercially as a stabilizer-plasticizer for vinyl floor goods, others for antimycotic and nematocidal activity. N-palmitoyl- and N-oleoyl-N'-methylpiperazine hydrochloride and many other of the amides have shown a broad spectrum of

antifungal and antibacterial activity. The finding that such activity closely parallels the water solubility or dispersibility of the compound will assist in the proper selection of derivatives for specific end-use applications.

Fairly complete lubricant evaluation data were obtained on three N,N-disubstituted amides: N,N-dibutyloleamide, N-oleoyl-4-propylpiperidine, and the morpholide of hydrogenated cottonseed fatty acids. The viscosity characteristics of N,N-dibutyloleamide at 100°, 210°, and -40° F conform to those set forth for lubricants for commercial jet airplane engines. The wear performance of all three amides was superior to that of the additive-free base jet engine lubricant di-2-ethylhexyl sebacate and of paraffin oil automotive lubricant controls but was inferior to that of controls containing anti-wear additives. These three amides exhibited no capabilities as anti-wear additives for the controls. Additional N,N-disubstituted amides meeting the viscosity requirements of lubricants are now being evaluated.

RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICRO-ORGANISMS AND NATURALLY OCCURRING TOXINS

A. Chemical Composition and Physical Properties

1. Properties of Derivatives of the Oil. Complete experimental solubility data were obtained for methyl stearate in acetone, n-hexane, toluene, and 1,2-dichloroethane. Sufficient solubility data were derived for eight other methyl esters of C_{16} to C_{18} fatty acids to permit their complete solubilities to be predicted by applying the reference isopleth correlation procedure to the curve for methyl stearate. Binary freezing point diagrams were constructed for 24 pairs of long-chain compounds. The data obtained help provide a sound basis for choosing the optimum solvents for the isolation and purification of fatty derivatives by solvent crystallization or by liquid-liquid countercurrent procedures. They also afford a basis for choosing the best reaction media in physical and chemical modification procedures and in the development of industrial processes to produce edible and inedible products from fats and oils in general.

B. Microbiology and Toxicology

1. Reactions and Effects of Cyclopropenoids. In research conducted under a grant to Boston University in Massachusetts, methyl sterculate was synthesized for the first time. By modification of this practical six-step procedure, methyl malvalate was prepared, including methyl malvalate labeled at the methylene carbon of the cyclopropenoid moiety. It should now be possible to prepare enough of this labeled isomer for metabolic studies. By appropriate modification of the procedure, additional labeled isomers of methyl malvalate might be prepared for metabolic studies important to our knowledge of possible adverse physiological effects of cyclopropenoids present in cottonseed oil.

The physiologically active cyclopropene moiety of the malvalic and sterculic acid groups in cottonseed oil was destroyed by heating under moderate conditions with a minute amount of finely divided palladium, which catalyzed the formation of conjugated fatty acid groups. The palladium treatment had no effect on the flavor, odor, or color of the oil. The cyclopropene moiety was also destroyed by hydrogenation, which produced only a small proportion of cyclopropanes. Hydrogenation converted the cyclopropenes into at least eleven different derivatives, whose structure and relative proportions were established. Improved methods devised for analyzing cyclopropenes include a micro titration procedure employing hydrogen bromide and a procedure involving reaction with silver nitrate. Additional chemical and physical properties of the cyclopropene acid groups were determined. Solubility in methanol at low temperatures and dilatometric properties were established for the methyl esters of the cyclopropene acids and their dihydro derivatives. Palladium treatment and hydrogenation provide satisfactory methods of destroying the physiologically active cyclopropenes of cottonseed oil, should that become necessary.

The biological effects of cyclopropenoids are being investigated in contract research at Ralston Purina Company, St. Louis, Missouri. Feeding of specially processed Halphen-negative cottonseed oils, a very slightly Halphen-positive cottonseed oil, and a soybean oil to laying hens for one year caused no significant pathological lesions and had no effect on the composition of the lipids of the heart, liver, plasma, or adipose tissues. Although lesions of leucosis and some atherosclerotic lesions were observed in many of the birds, histopathological examination revealed no pathology that appears to be related to the dietary treatments. Laying hens fed a Halphen-positive, refined cottonseed oil and a soybean oil that was supplemented with Sterculia foetida oil had increased levels of saturated fatty acids and decreased levels of unsaturated fatty acids in the lipids of the liver and heart and of adipose tissues of abdomen and gizzard. Similar studies with reproducing rats revealed that none of the above oils had a detrimental effect on reproduction or any significant effect on the composition of the lipids of the heart, liver, plasma, or adipose tissues. Physiological responses to the specially processed cottonseed oils were not significantly different from those to the soybean oil control.

Related research is being conducted under a P. L. 480 grant to the Division of Food Preservation, Commonwealth Scientific and Industrial Research Organization, Ryde, New South Wales, Australia. Radioactive cyclopropene fatty acids were prepared by incubating slices of young seed of plants of the order Malvales with labeled methionine. The structure of the yolk and vitelline membrane of eggs from hens ingesting cyclopropenoids was studied by optical and electron microscopy. In hen liver preparations, sterculic and malvalic acids inhibited the desaturation of all the fatty acids from C_{12} to C_{22} at the 9,10- position, but only slightly affected desaturation at the 10,11- and 11,12- positions. Sterculic acid was the more effective. The fact that maximum desaturation occurred with the C_{14}, C_{17}, and C_{18} fatty acid substrates suggested the presence of at least two desaturating systems.

It is suggested that desaturation is inhibited because sterculic acid and/or its CoA derivative forms a C-S bond between the C_9 or C_{10} group of sterculic acid and a thiol group in the desaturation site of the enzyme. The inhibition of this enzyme system may be the key to the observable effects of dietary cyclopropenes.

2. Detection, Estimation, Prevention, and Elimination of Aflatoxins. An improved method for estimating aflatoxins in cottonseed products was studied collaboratively by 12 laboratories and then adopted as a first action method of the Association of Official Analytical Chemists. The method showed good agreement between visual and densitometric estimates of aflatoxins on thin layer plates. In incubation experiments, seed from cotton plants treated with two commercial fungicides effective against Verticillum wilt failed to exhibit any resistance to mold attack and aflatoxin elaboration by A. parasiticus. Aflatoxin primary standards can be stored for at least one year in either benzene or chloroform solution at -18° C (0° F) with little or no deterioration. Storage at 28° C leads to considerable deterioration.

Fundamental research on aflatoxins is being conducted in a P. L. 480 project at Nagoya University, Anjo, Aichi, Japan. Scientists there are investigating the biochemical mode of action of aflatoxins and their biodegradation by plant cell systems.

Aflatoxin-contaminated cottonseed meal was extracted with two solvent systems, isopropanol/water and acetone/water, in a small scale countercurrent extractor. The acetone/water solvent not only removed aflatoxins more effectively but extracted less meal solids. These considerations are important in selecting a solvent for the commercial removal of aflatoxins from contaminated cottonseed meals to permit their use in feeds without hazard and to increase the economic return. Ability to utilize the extracted solids (other than aflatoxins), preferably in animal nutrition, would facilitate commercialization of a practical extraction process. Aflatoxins were completely eliminated from the extracted meal solids by heating a water solution of the solids with formaldehyde and sodium hydroxide. This treatment may allow use of the extracted solids in animal feeds, or, if economically justifiable, permit disposal of the solids without the danger of pollution from aflatoxins.

Ammoniation processing conditions for lowering aflatoxin levels in cottonseed meal from 350 ppb to 4-5 ppb were 45 psig ammonia pressure, 200° F, 10-15% meal moisture, and 30 minutes reaction period. For methylamine processing of the same cottonseed meal to yield products containing 3-7 ppb aflatoxins, the conditions were atmospheric pressure, 2.0% methylamine (with or without 1.0% sodium hydroxide), 212° F, 15% meal moisture, and 30 minutes reaction period. Sufficient quantities of two ammoniated meals and two methylamine treated meals have been prepared and submitted to WU for rat feeding tests. These treatments also show promise of being developed into commercial processes to decontaminate aflatoxin-containing cottonseed meals to permit their use in feeds.

3. Elimination of Salmonella. The literature on Salmonella was reviewed, particularly with respect to oilseed products. Preliminary surveys were made to identify the microbiological flora of cottonseed products being processed in two oil mills. Four sets of samples were taken, timed to obtain materials as they progressed through the mills. In both mills, the total plate counts of samples taken before cooking were in the millions, but counts after cooking and pressing were below 5,000. However, some products were recontaminated between cooking and bagging. Salmonellae were found in one environmental sample and in the finished meal at one plant. This research is particularly important because cottonseed meals, flours, and concentrates may soon be produced commercially for use in foods.

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AREA 3 - PEANUT UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
406	New and improved food products from field crops			
	Chemical composition and physical properties	3.7		3.7
	Flavor	1.4		1.4
	Technology--process and product development	0.8		0.8
	Subtotal	5.9		5.9
702	Protect food supplies from harmful microorganisms and naturally occurring toxins			
	Microbiology and toxicology	6.5		6.5
	Subtotal	6.5		6.5
	TOTAL	12.4		12.4

Domestic program supplemented by P. L. 480 funds in 1 country totaling 11,898 U.S. dollars equivalent per year (Spain).

Problems and Objectives

Despite the surplus of peanuts, their price is relatively high. The domestic crop is used primarily in foods such as peanut butter, confections, bakery items, and roasted nuts. However, in recent years, much of the crop has been dried and cured artificially, partly to afford protection from contamination with mycotoxins but with the result that peanuts and their products do not always have the same desirable flavor as peanuts cured slowly in the field. Information is therefore needed on the relation of chemical constituents of peanuts to the flavor, aroma, and other properties of the processed products. In addition, new and improved products must be developed to extend domestic markets. Basic and applied research on peanut proteins is a particularly important requisite to this expansion. To assure that peanuts will continue to be utilized in food and feed products, they must be protected from contamination by fungi and mycotoxins.

Major objectives of the research are:

1. To identify chemical sources of the characteristic roasted peanut flavor and aroma.

2. To develop new and improved products and processes.

3. To expand domestic markets by tailoring products to meet preferences of the consumer.

4. To insure the safety and wholesomeness of peanuts and peanut products.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Properties and Reactions of the Proteins. Proteins extracted from peanuts that had been defatted with various organic solvents (acetone, hexane, carbon tetrachloride) decreased in solubility. The most drastically altered fractions were the water-soluble albumins and buffer-soluble conarachin. Arachin was affected most by acetone extraction. Peanut proteins were altered by roasting, depending on the initial water content of the seeds. However, arachin remained antigenically active up to 155° C. Investigations of nitrogen metabolism revealed that the nitrogen storage pool in the peanut, γ-methylene glutamine, was at its maximum concentration in seedlings that had germinated for 10 days. A nonspecific hemagglutinin was purified and identified from salt extracts of the peanut. A new microcalorimeter using semiconductor elements was completed and is being used to study the thermodynamic properties of peanut proteins. Information obtained should be valuable in determining processing conditions that yield protein isolates and concentrates of the highest quality, such as those being used in artificial milk-type beverages and other nutritional foods.

The effect of moisture in protecting the peanut protein during roasting was verified for Valencia peanuts, both shelled and unshelled. The shell also tends to protect the protein during roasting. Moisture also had a protective effect in shelled, Texas-grown, Spanish-type peanuts roasted with and without prior drying. The protective action of fat on the peanut protein during roasting was demonstrated with the Spanish-type peanuts. When isolated peanut protein was heated in absence of sugars, moisture did not have a protective effect. Scientists at the University of Granada in Spain, where this research is being conducted under a P. L. 480 grant, have interpreted these results to mean that the moisture protects by chemically--rather than physically--inhibiting the reaction of the sugars with the protein. Preliminary palatability tests indicated that peanuts roasted in a moist atmosphere are quite acceptable.

2. Properties of the Lipids. Ureide metabolism studies in the peanut and castor bean revealed that these enzymes may be particulate bound. Acid proteinase isolated and purified from Cannabis sativa was associated with the aleurone grain fraction; further experiments indicated that it too may be lipid bound. The acid lipase isolated from castor bean had position specificity for the first and third ester linkages; it did not hydrolyze the secondary ester position. Study of the effect of various solvents on the ultrastructure of spherosomes showed that the acetone-hexane-water azeotrope extracted more lipoidalphosphorus from cottonseed than did the classical solvent (chloroform-methanol) and, in so doing, considerably deranged the structure of the spherosomes. Miscella from cottonseed was blanched with ferric chloride-acetone solution followed by filtration. By clarifying the mechanism of lipid and protein metabolism and its relationship to protein-lipid interaction, the research will aid in determining the proper conditions for processing peanuts and other oilseeds.

B. Flavor

1. Factors Affecting Flavor and Aroma of Processed Products. Laboratory procedures were developed for isolating a concentrate of the volatile components associated with flavor and aroma of freshly roasted peanuts. The concentrate was prepared under mild conditions without use of solvents or reagents, thus minimizing the formation of artifacts. Gas chromatography effectively separated the mixture into a number of fractions, some of which were still mixtures, and also gave evidence of a large number of others present only in trace amounts. Some of the major components contributed grassy notes, a buttery note (diacetyl), or a roasted note. The fraction having the aroma most suggestive of freshly roasted peanuts was very unstable and may be a mixture. Its properties were suggestive of an alkyl-substituted dihydropyrazine. Development of procedures to isolate and analyze flavor components should facilitate elucidation of changes associated with staling. Results to date indicate that staling is at least partially chemical in nature.

C. Technology--Process and Product Development

1. Improved Low-Fat Peanut Products. Laboratory data were obtained to determine the effect of pressing temperature and moisture content of peanuts on oil removal and other characteristics of the product. As the temperature increased from 40 to 100° F, more oil was removed and the amount of moisture required for maximum oil removal decreased. Peanut breakage during pressing decreased with increase in temperature or in moisture. The texture of partially defatted oil-roasted peanuts varied with moisture pickup during the expansion of the pressed peanuts before roasting. Exploratory work showed that addition of enzymes such as papain helped to improve texture. Storage tests showed that oil-roasted, partially defatted peanuts kept satisfactorily for 12 months under nitrogen.

RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICROORGANISMS AND NATURALLY OCCURRING TOXINS

A. Microbiology and Toxicology

1. Detection, Estimation, Prevention, and Elimination of Aflatoxins. When colored mutants of A. flavus and A. paraciticus were produced by graded exposure to ultraviolet light, their ability to produce aflatoxins was markedly changed. The destruction of aflatoxins in alkaline soapstock during acidulation is enhanced by pH levels in the range of 1 to 2 and by temperature in the range of 80 to 100° C. Plant introductions of reputedly aflatoxin-resistant peanut varieties grown in the U. S. did not resist attack by mold and production of aflatoxin.

Gas-liquid chromatography of head space gas from high quality and from mold damaged peanuts seems promising as a rapid technique for detecting mold attack. GLC peaks appear to be characteristic of mold per se and of mold attack.

Aflatoxin-contaminated peanut meals were treated with heat in the presence of moisture and various reagents in an effort to lower the aflatoxin content. Of the reagents tested, only calcium hydroxide offered promise of practical application. Development of an economical, large-scale process for inactivation of aflatoxins in such meals would permit their use without hazard in animal feeds rather than their uneconomical diversion to fertilizer. Earlier work had revealed that aflatoxins could be extracted from contaminated peanut meals with 80% isopropanol and that the aflatoxins appeared unchanged in the extracts. Sunlight irradiation of the liquid extract inactivated the aflatoxins, and hydrogen peroxide treatment of the extract in water solution partially inactivated the aflatoxins. Development of a practical method for removing aflatoxins from the extracted solids would allow them to be used in animal feeds and would also improve the economy of the extraction process.

In addition to the treatments described above, the use of anhydrous ammonia to inactivate aflatoxins in peanut meal may be promising for commercial application. In general, the processing conditions found adequate to reduce the total aflatoxin content of peanut meal from 120 ppb to 5 ppb or below were: ammonia pressure, 30 psig; temperature, 200° F; meal moisture, 15%; and time, 15-30 minutes.

Publications - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

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RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICROORGANISMS AND NATURALLY OCCURRING TOXINS

Microbiology and Toxicology

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AREA 4 - CITRUS UTILIZATION

USDA and Cooperative Program

Problem Area No.	Title and Activity	Scientist Man-Years (Estimated) Intramural	Extramural	Total
403	New and improved fruit and vegetable products			
	Chemical composition and physical properties		1.4	1.4
	Flavor	13.1	0.6	13.7
	Color, texture, and other quality factors	1.1		1.1
	Technology--process and product development	2.2		2.2
	Subtotal	16.4	2.0	18.4
901	Alleviate soil, water, and air pollution			
	Technology--process and product development	2.2		2.2
	Subtotal	2.2		2.2
	TOTAL	18.6	2.0	20.6

Problems and Objectives

Advances in the citrus and subtropical fruit industry are needed to utilize the already large but increasing production of these fruits to the economic advantage of growers, processors, and consumers. Research should be conducted not only to relate chemical components of citrus to its natural flavor and color but also to solve problems caused by bitterness and other off-flavors in grapefruit and oranges. New products should be developed to use more fruit, to attract consumers, and to reduce shipping costs. A particularly important aspect is utilization of a larger proportion of the fruit for food--as in comminuted whole citrus products--to reduce the problem of pollution from wastes and to obtain versatile products at lower cost. Processing procedures and equipment must also be improved. In addition, rapid, sensitive, and economical tests of quality must be devised to assure that the most desirable qualities of citrus and subtropical fruit are conveyed to the consumer.

Important goals of the research are:

1. To develop new and improved products from citrus.

2. To identify the sources of undesirable flavors in citrus and to develop methods to prevent them.

3. To improve processing methods to preserve or enhance the natural flavor, color, and other desirable properties of citrus products.

4. To expand markets by tailoring products to meet the needs and preferences of consumers.

5. To reduce pollution from citrus wastes by using more of the whole fruit for food.

Progress - USDA and Cooperative Program

RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS

A. Chemical Composition and Physical Properties

1. Relation of Ribonucleotides to Consumer Acceptability of Processed Products. In grant research conducted at the Florida Agricultural Experiment Station in Gainesville, ribonucleotides in citrus are being evaluated for their potential in affecting the appeal of processed products to the consumer, controlling changes in the fruit, and providing an index of quality.

2. Estimation of Peel Solids. Development of an organic acid index to assess the amount of peel solids in citrus products is the goal of

contract research conducted at the Stanford Research Institute, South Pasadena, California. Data obtained in 1968 for California Valencia oranges and Marsh grapefruit picked at intervals throughout the April to October growing season will be combined with 1969 data before being analyzed. The amount of total free acids; total combined acids; and free and combined oxalic, malonic, succinic, malic, and citric acids in segment juice, rag, peel juice, and pressed peel was determined for each batch of fruit. Similar data were obtained for early-, mid-, and late-season California Valencia oranges after storage at 50°F for 0, 2, 10, and 30 days. Oxalic acid was never found in segment juice but always (in combined form) in rag and pressed peel of oranges and sometimes in rag and pressed peel of grapefruit. No systematic changes in oxalic acid content could be attributed to maturity or to storage. This work therefore confirms the earlier conclusion that the proposed oxalate index appears feasible for oranges but not for grapefruit. The index should be applicable to fruit of any maturity and also during storage. No other acid showed promise as a peel index.

B. Flavor

1. Improved Flavor and Quality. Enzyme reactions are being evaluated for their potential in enhancing the flavor of citrus products. Orange and grapefruit juice cells contain oxidation-reduction enzymes that control equilibrium between hydroxyl and carbonyl compounds. Holding oranges and grapefruit for less than a day in heated carbon dioxide and nitrogen chambers shifted the reaction toward the hydroxyl compounds and reduced acidity of the fruit 10 to 20%. Since total soluble solids increased, the Brix/acid ratio of the treated fruit was between 1 and 2 units higher than that of untreated fruit. These findings should lead to commercial development of a rapid maturation process that would be advantageous to both processed and fresh fruit operations.

During the processing of citrus juice, heat is used to pasteurize it and to stabilize appearance and flavor. However, if heating were not necessary, the product would be similar to fresh citrus juice. Preliminary review of the theory and practice of processing fruit juices indicated that the alternatives used to satisfy all the requirements for heat included cold chemical pasteurization, depectinization to stabilize appearance, and reduction of atmosphere to stabilize flavor. The first two of these alternative procedures have been applied successfully to citrus.

In research on the composition of essential citrus oils, the seven unknown α,β-unsaturated aldehydes isolated from the carbonyl fraction of orange peel oil were characterized. They were found to be the α,β-disubstituted acroleins that result from the dehydration of the various mixed and self aldol condensation products of octanal, nonanal, and decanal. Although these α,β-unsaturated aldehydes themselves seem to contribute little to orange flavor, they may be important because of their close relationship

to the abundant saturated straight-chain aldehydes octanal, nonanal, and decanal, which are commonly considered to be important contributors to orange flavor. Samples of essence from various orange and grapefruit peel products were similar in composition to essence derived from juice, an indication that peel essence can be used as an alternate to juice essence for flavor fortification of citrus products. Since the flavor of orange does not appear to result from one particular compound, a survey was made of the known major constituents of orange peel oil and eight of these were selected as the major contributors to orange flavor.

Of the eight compounds considered important to orange flavor, only sinensal is not a readily available product whose flavor and odor properties are relatively well understood. The flavor potency of sinensal is greater than that of nootkatone and is fairly high in comparison with that of most other food flavoring compounds. Terpeneless orange oil was prepared by eight different procedures to determine the effect of various separation methods--such as distillation, solvent extraction, and chromatography--on the quality of the oil. In all of the procedures, there was a significant loss in quality. Low temperature liquid adsorption chromatography of orange oil produced a product that differed considerably quantitatively but not qualitatively from the product obtained by the usual room temperature liquid adsorption chromatography. A promising method was developed for analyzing orange essence on a flame ionization gas liquid chromatograph. A number of compounds new to citrus oils were isolated from the "carbonyl" fraction of grapefruit oil, including a group that seem to be related to nootkatone. One was identified as isonootkatone.

Recently initiated research conducted in cooperation with the Florida Citrus Commission and the Western Utilization Research and Development Division is directed toward developing flavor concentrates to improve foam-mat dried and other citrus products. A number of distillation, liquid-liquid extraction, and fractionation methods have been applied to citrus juice byproducts such as peel, peel oil desludger effluents, and ground whole fruit. These materials may serve as sources of components to enhance the flavor of instant orange juice and other dehydrated products.

2. Prevention of Deterioration of Flavor. Samples of frozen concentrated orange juice commercially produced over a period of 15 years were analyzed for each of the five flavones identified as major components of the bitter neutral fraction of benzene extract of peel juice. The flavones occurred in proportions similar to those found in peel juice, but their total concentration did not exceed 7.1 ppm. Since this period included two major freezes and a program of substantial changes in juice yields, both of which affected juice quality, and since even 24 ppm cannot be tasted in orange juice, it was concluded that these flavones do not contribute significantly to the bitter flavor sometimes detected in the juice. Some medical and biochemical research institutions have recently expressed interest in one of the flavones, nobiletin. A process was devised to

prepare it from tangeretin, which is easily obtained. Tangeretin and reagents are being accumulated to permit pilot-plant preparation of sufficient nobiletin to supply the needs of these institutions.

Phospholipids from commercial citrus juices were highly susceptible to degradation at elevated temperatures. Breakdown of phospholipids by enhanced thermal and/or enzymatic activity increased the quantity of free fatty acids. Compared to bound acids, free acids were more susceptible to oxidation. The oxidation of these free acids results in the formation of scissile products possessing adverse organoleptic properties. Fatty acid compositional studies conducted on the juice and seeds of six citrus species showed no apparent relationship between the degree of fatty acid unsaturation and the susceptibility of a juice to develop off-flavor. These studies were prompted by the observation that some citrus juices are more susceptible to deterioration than others; the possible difference in proneness to rancidity may lie in the unique fatty acid profiles. Citrus possesses an extremely complex fatty acid pattern. The number of different juice acids observed in the C_{12} - C_{26} region ranged from 81 (Key lime) to 102 (Eureka lemon), and the number of seed acids ranged from 62 (Valencia orange) to 68 (Key lime and Eureka lemon). Thirty-eight different iso and 26 anteiso acids were observed for the first time in edible plant material in concentrations ranging from less than 0.001% to more than 1%.

In contract research at Ohio State University Research Foundation, Columbus, Ohio, a number of variables are being studied for their effect on browning of sugar-amino mixtures in aqueous solutions; this nonenzymatic browning may have an important role in the development of off-flavor in orange juice powder. A number of model systems simulating orange juice powder were prepared, either with different chemical additives used or with specific components removed. When the model systems were stored at elevated temperatures, the degree of darkening varied with composition and type of additive. These systems are being studied for the presence of nonenzymic browning intermediates, and the analytical results are tested for correlation with composition. Gas-liquid chromatographic methods have been developed for determining gross patterns, which will be compared between systems to determine the extent of formation of nonenzymic browning intermediates.

3. Bitter Constituents and Related Components of Grapefruit. For the third season, grapefruit from early blossoming had a higher bitter flavanone content than did fruit from later blossoming. The leaves of the tree contributed a major portion of the bitter components present in the fruit. Rapid accumulation of bitter components in the grapefruit occurred when leaves were rapidly proliferating. In grafted Redblush grapefruit, very high temperatures inhibited synthesis or speeded up destruction of the red pigment lycopene; fruit grown outside under a shade had a higher

concentration of lycopene than did those grown under natural conditions. Growth regulators applied to grafted Redblush grapefruit grown in cool and warm environments could not offset the effect of the cool temperatures on the pigments, but in the warm environment several of the growth regulators caused lycopene concentration to increase.

C. Color, Texture, and Other Quality Factors

1. Extracts from Peel to Enhance Color. The color extraction procedure reported previously, consisting of extraction of ground wet orange peel with n-hexane followed by vacuum steam distillation and concentration of the color extract, was applied to tangerines, tangelos, Temple and navel oranges, and the principal late season variety, Valencia. Highest yield and best color quality were obtained in extracts from Pineapple and Valencia oranges. Good yields of color were obtainable from peel that had been deoiled, as well as from flavedo and coarsely ground whole peel. The better color extracts were effective at a dilution of 1:250 parts in raising the USDA grade standard by one score in standard orange juice products. Thus it may be possible to obtain concentrates to enhance the color of citrus products directly from processing wastes and byproducts.

D. Technology--Process and Product Development

1. Control of Bitter Constituents in Citrus. Contract research on debittering grapefruit sections and juice by the use of naringinase at relatively low levels was completed by the Florida Agricultural Experiment Station at Lake Alfred. Two enzyme preparations were evaluated, and techniques for their use were developed in in-plant pilot-scale operations. Addition of 0.1% naringinase to chilled grapefruit sections reduced bitterness fairly rapidly even though jars were stored at 32° F. Addition of 0.005% Japanese naringinase lowered naringin values 50% in 17 days' storage at 32° F; this amount added to sections stored at the same temperature also prevented naringin crystals from being deposited. High naringin content in grapefruit concentrate was reduced to acceptable levels by adding either 0.1% or 0.05% naringinase to reconstituted single strength juice and holding 60 minutes before canning. In preference testing, the debittered product was rated as slightly better than normal juice.

In other research on bitter components, an exploratory screening of citrus juices for both naringin and limonin was conducted. Naringin content was proportionately less than previously reported for grapefruit when estimated by the generic Davis test for flavanone glycosides. Naringin was not found in any of the orange or grapefruit-tangerine hybrids examined. Limonin was found in the juice of all varieties of citrus examined at early maturity. No orange variety contained enough limonin to appreciably affect flavor unless the fruit was very immature or had been damaged by freezing weather. Marsh grapefruit juice contained three times as much limonin as Duncan when harvested in January, but it had disappeared from both by May. Grapefruit-tangerine hybrids contained varying amounts of limonin but did not

contain naringin. The Murcott was the only hybrid orange tested that reached the threshold concentration of limonin, 8 ppm. The presence of limonin in citrus hybrids and in freeze-damaged fruit has not been demonstrated previously.

2. New and Improved Products from Citrus and Subtropical Fruit. Off-flavors forming in stored instant orange juice (IOJ) were found to be due to at least five different nonenzymic browning intermediates, which have been isolated and identified. Fructose, glucose, or ascorbic acid could serve as sources for these components. Preferred oil levels in IOJ were higher than normally used in frozen concentrated orange juice (FCOJ). Concentrated orange juice essence enhanced the flavor of IOJ. However, two to five times as much essence was needed for IOJ as would normally be added for FCOJ. New instant citrus juice powders mixed with other juices such as strawberry and pineapple were developed. Instant juice products sweetened with sugar or cyclamate were prepared. A new product, orange juice as an edible confection in tablet form, was also developed in the research which was conducted in cooperation with the Florida Citrus Commission and the Western Utilization Research and Development Division.

Freeze-drying rates and extent of moisture removal were compared in model systems (composed of sugar mixtures and citric acid) and in orange and grapefruit juices at different beginning concentrations. Finely ground samples dried at a more rapid rate and more completely than did those coarsely ground. Although this effect was observed in all systems, it was most pronounced in orange juice. The effect of particle size was much more influential on highly concentrated starting materials than on single strength juices.

A freeze-dried avocado salad product recently prepared has not only acceptable color and flavor but also storage stability sufficient for commercial distribution. Products packed in nitrogen or under vacuum retained acceptable flavor characteristics for 48 weeks when storage temperatures did not exceed 40°F; acceptable flavor characteristics were retained as long as 16 weeks at 68°F. The optimum moisture level for preserving quality was 2.0 to 3.4%. Peroxide formation preceded flavor deterioration in material stored in air. Analysis of the lipids and carotenes of the stored material showed no significant decrease in the concentration of the unsaturated fatty acid portion of the lipids for periods up to 48 weeks; however, the carotene content decreased rapidly. Study of a model system suggested that carotene breaks the chain reaction typical of peroxide formation in unsaturated fatty acids and thus causes overall stabilization of the lipids in freeze-dried avocado salad stored in air.

RPA 901 - ALLEVIATE SOIL, WATER, AND AIR POLLUTION

A. Technology--Process and Product Development

1. Comminuted Whole-Fruit Products. A process for the preparation of an edible citrus puree, utilizing 85 to 90% of the whole fruit (only rag, seeds, and scaly peels rejected), was developed on a laboratory scale (50 lbs. fruit). This puree would utilize approximately 35% more of the whole citrus fruit for human consumption than do present processes for manufacturing citrus juice and juice products. Drinks containing 10% of the whole fruit puree were judged to have excellent flavor, color, and consistency. The utilization of grapefruit puree required an additional step of enzyme debittering. Heat processed canned drinks prepared from the whole orange puree were judged to have maintained acceptable characteristics after one year's storage at 68°F.

Publications - USDA and Cooperative Program

RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS

Chemical Composition and Physical Properties

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Technology--Process and Product Development

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General

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AREA 5 - VEGETABLE UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
403	New and improved fruit and vegetable products			
	Flavor	2.1		2.1
	Technology--process and product development	7.9		7.9
	TOTAL	10.0		10.0

Problems and Objectives

The market for fresh vegetables has suffered from the effects of rapid spoilage, seasonal surpluses, and increasing demand for convenience foods. Stable, attractive, and convenient processed vegetable products must therefore be developed. However, much research is needed to solve problems incurred in the processing. For example, although most of the cucumber crop is brine-cured, spoilage during curing frequently causes high losses. To increase the utilization of dehydrated sweetpotatoes, their shelf-life should be extended and new products developed to combine the flakes with other foods. Celery, already an important flavoring ingredient, could become much more widely used if factors responsible for variations in the intensity of flavor could be controlled during processing and if more convenient products were developed. To improve processed vegetables, there is also need to determine the effect of climate, soil, cultural practices, and variety upon the raw material, particularly for vegetables like tomatoes, in which color, flavor, and texture are frequently poorer when they are grown in warm instead of temperate regions.

More specific objectives of the research are:

1. To identify the effect of different characteristics of raw vegetables on quality of the processed products.

2. To improve processes for fermented vegetables, particularly cucumbers.

3. To modify and enrich products from sweetpotato puree and flakes.

4. To develop products having improved natural celery flavor.

5. To develop new and improved products from other southern-grown vegetables, such as tomatoes and carrots.

Progress - USDA and Cooperative Program

RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS

A. Flavor

1. Prevention of Deterioration of Quality. There is a relationship between development of off-flavor and degradation of carotenoids in some dehydrated vegetable products. Although the role of the carotenoids in oxidation or deterioration is not known, off-odor evidently arises from compounds other than carotenoids. By use of radioactive β-carotene, a method was devised for studying carotenoid autoxidation in precooked dehydrated sweetpotato flakes. About 20% of the carotene was oxidized in thirty days at room temperature in the presence of air. Thereafter the rate was very slow although oxygen was not limiting. Among the first

products of autoxidation were steam volatile colorless carbonyls, which were subsequently oxidized to acids and carbon dioxide. This research is conducted in cooperation with the North Carolina Agricultural Experiment Station.

B. Technology--Process and Product Development

1. Fermented Cucumber and Other Vegetable Products. A softening enzyme, polygalacturonase, was extracted from the tissue around the seeds of ripe pickling cucumbers. This enzyme may cause soft-centers in brine stock. Conditions affecting its activity were investigated. Myprozine, a commercial fungistatic agent, inhibited the growth of eight species of brine yeast tested in brined cucumber fermentations. The agent has potential for reducing bloater formation due to gaseous fermentations, providing its use is approved by the FDA. Extensive tests were initiated on methods for controlling the fermentation of cucumbers, particularly by pure culture techniques. Various phases of the research are conducted in cooperation with the Pickle Packers International, Inc., and the North Carolina and Michigan Agricultural Experiment Stations.

2. New and Improved Sweetpotato Products and Processes. Changes in sugar and α-amylase were evaluated in lots of Centennial and Goldrush sweetpotatoes during storage. A twofold increase in sucrose was observed in all lots after 70 days' storage. The formation of α-amylase varied between lots of the same variety, but the increase was generally slower in the Centennials. No relationship between the rate of increase or amount of sugars and α-amylase formed was evident. Sweetpotato flavor concentrates prepared by hot-water extraction of fresh roots were of the same intensity as those from stored roots. A nutritionally improved sweetpotato mix for pies or casseroles was developed by dry-blending flavoring ingredients with ground precooked flakes. After one year's storage, the nitrogen-packed samples of dry-blended mix rated 7.3 on a nine-point scale, whereas the air-packed samples rated 6.9. Protein products added to cooked sweetpotato puree proved compatible for drum drying. However, as the amount of protein increased, the flavor of the product changed and the amount of water needed for reconstitution decreased. Cooperation has been maintained with the Louisiana and North Carolina Agricultural Experiment Stations.

3. More Flavorful Dehydrated Celery Products. A continuous atmospheric distillation method for recovering a high-quality celery essential oil in good yield has been developed. The essential oil obtained by this method, in comparison with celery essential oil obtained by atmospheric batch distillation, more closely resembles the aroma of fresh celery. Chemical analyses of the essential oils obtained by the continuous atmospheric and the atmospheric batch distillation methods showed quantitative and qualitative differences between the essential oils, especially with respect to the carbonyls. These data suggest that certain carbonyl compounds had chemically decomposed during batch distillation, which requires the feed material to remain at elevated temperature for a prolonged period. The improved

method subjects the feed material to high temperature for a relatively short time, therefore reducing the chance of producing artifacts and off-flavors. From chemical analysis, eight terpene and sesquiterpene hydrocarbons and 12 aliphatic and terpene alcohols were identified as constituents of celery for the first time. Work on the carbonyl constituents has not been completed; however at least eight unreported carbonyl compounds have been identified.

4. Improved Tomato and Other Vegetable Products. In cooperation with the Texas Agricultural Experiment Station, Crops Research, and industry, innovations in food technology are being applied to the development of improved products from southern vegetables. Work is underway to determine the quantity and quality of pectic substances in tomatoes and to relate these findings to processing characteristics. Samples of five varieties of tomatoes were prepared for determination of alcohol-insoluble solids; crude fractionation of the pectic substances according to solubility in water, acid, and oxalate; and gel filtration of the various pectin fractions. A fast, clean, and possibly economical method was developed for peeling tomatoes in liquid nitrogen with minimum loss of trim and peel and significant retention of the layers of highly pigmented cells just beneath the peel. Losses of trim and peel were reduced approximately 50%, and lycopene losses were similarly reduced.

Other research on southern vegetables is being conducted with the assistance of the same cooperators. In these investigations, a coagulum that often forms in heat-processed carrot juice was eliminated by heating the whole carrots in a weak food-grade acid before the juice was extracted. The treatment also increased the amount of juice extracted; this slightly acidified juice had excellent flavor, and the orange color was intensified. Another advantage is that existing commercial canning equipment can be used. A second phase of the research concerns Brassica carinata, an excellent canned or frozen green leafy vegetable crop. This plant was introduced into the United States from Ethiopia as a possible source of edible oil from the seed. The flavor of the cooked leaves is milder than that of collards without the pungency of mustard. In comparison with spinach, the oxalic acid content is much less and the percent calcium about the same. The plants can be machine-harvested. In other studies, tomato samples were prepared for a study of the effect of climatic conditions on the formation of lycopene and carotene in the fruit.

Publications - USDA and Cooperative Program

RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS

Chemical Composition and Physical Properties

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AREA 6 - NAVAL STORES UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
401	New and improved forest products			
	Chemical composition, physical properties, and structure	0.2		0.2
	Technology--process and product development	12.9	3.3	16.2
	TOTAL	13.1	3.3	16.4

Problems and Objectives

Naval stores are unusual agricultural products in that they are used almost exclusively as chemical raw materials. Although rosin, turpentine, and pine gum consist of organic compounds with unique chemical structures that are difficult to duplicate synthetically, these naval stores products face increasing competition for markets from products derived from petroleum and coal tar. Research is needed to retain or expand industrial markets for naval stores, particularly in large-volume outlets such as polymers, plastics, elastomers, resins, plasticizers, surface coatings, adhesives, textile finishes, odorants, and agricultural chemicals. Although about one-third of the rosin produced in this country is already exported, research to convert rosin to more expensive derivatives would not only increase the value and the amount of rosin exported but also benefit domestic markets.

Major objectives of the research are to develop:

1. Basic knowledge of the composition and properties of pine gum, rosin, turpentine, and their derivatives.

2. New and improved chemical intermediates from rosin, resin acids, terpenes, and pine gum.

3. New and improved industrial products--particularly polymers such as polyurethanes, polyesters, and polyamides--from rosin, turpentine, and pine gum.

Progress - USDA and Cooperative Program

RPA 401 - NEW AND IMPROVED FOREST PRODUCTS

A. Chemical Composition, Physical Properties, and Structure

1. Composition and Properties of Pine Gum, Rosin, Turpentine, and Derivatives. The preliminary examination of stump wood of ponderosa pine from Arizona and New Mexico was completed. The results indicate that the turpentine, pine oil, and rosin from this wood would require further processing before they could be substituted for the present commercial products. Improved methods of analysis developed in the course of this work now make it possible to detect and in some cases isolate previously undetected components of pine gum and rosin. For example, neutral compounds such as the alcohols and esters of resin acids were detected for the first time in gum rosin, and other neutral compounds were isolated. Several aldehydes of resin acids were also detected in gum rosin. It is now possible to compare qualitatively and quantitatively the turpentines, pine oils, and rosins from various species of pines as well as from different commercial sources.

B. Technology--Process and Product Development

1. Chemical Intermediates from Rosin, Resin Acids, Terpenes, and Pine Gum. Research is continuing on the application of photochemical reactions to naval stores products to produce potentially useful chemical intermediates. Each of the abietic-type acids was found to undergo a different type of reaction in alcohol solution when exposed to 2537Å light. Some of these reactions were not like any known photochemical reaction. Laboratory procedures were developed for the photochemical addition of water and primary alcohols to abietic acid or methyl abietate. Rates of reaction and product distributions varied with the alcohol used. The products had unique structures and should have unusual properties. Secondary and tertiary alcohols did not add. Photolysis in aprotic solvents gave nonvolatile products and may offer a route to resin acid dimers. Methyl neoabietate reacted with methanol but gave abnormal products. Methyl levopimarate underwent intramolecular rearrangement so rapidly that no addition of methanol occurred. The conjugated monocyclic terpenes α-terpinene and α-phellandrene rapidly yielded trienes, which reacted with dienophiles and should be polymerizable. β-Phellandrene and 2,4(8)menthadiene reacted more slowly to give nonconjugated products. The pinenes did not react. These findings do much to show the scope of photochemical reactions of resin acids and terpenes.

In contract research at Battelle Memorial Institute, Columbus, Ohio, three different types of acid catalysts have been evaluated for the dimerization of some pure resin acids, gum rosin, and selected gum rosin modifications. When sulfuric acid was used as catalyst, high yields (90%) of dimeric species were obtained from abietic acid, the major resin acid present in gum rosin. Good yields of dimers were also obtained from gum rosin when based on the abietic-type acids present. The promising process developed for dimerizing rosin should be of considerable interest to current and potential producers of rosin dimer. Emphasis in continued research will be on the development of a practical process for separating the rosin dimer from other components of the reaction mixture.

A study of the chemistry of levopimaric acid transannular peroxide was completed. This product is readily obtained by photosensitized oxidation of levopimaric acid, the unique resin acid that is present to the extent of 25 to 38% in pine gum. The research established this peroxide as a versatile chemical intermediate for the chemical industry. Most of the compounds prepared in this work as well as chemically modified derivatives of photosensitized-oxidized pine gum were tested as agricultural chemicals (fungicides, bactericides, nematocides, herbicides, insecticides) at the University of Florida. A number of them showed activity.

Research is in progress to prepare di- and polybasic acids from rosin for use in making or modifying condensation polymers. The entire process for the preparation of polyesters from gum rosin reacted with beta-propiolactone or acrylic acid is under examination in order to establish procedures

for producing the best possible products at lowest cost. Some of these polyesters have shown good potential as rubber tackifiers and in other applications. Chromate oxidation of gum rosin and of pure resin acids is being investigated for its potential in the production of di- and polybasic acids.

High-temperature rearrangements of gum rosin, resin acids, and their derivatives are being investigated as a basis for producing new materials with industrial potential. The structures of the four products obtained on heating methyl levopimarate at 200°C in the presence of a catalytic amount of base were elucidated. All four products are open ring compounds: two of these result from the cleavage of one ring, and two others from the cleavage of two rings. In all cases the third ring is aromatized. This represents the first example of the controlled opening of the phenanthrene ring of the resin acid series. The mixture of open ring compounds was ozonized followed by oxidation to give a mixture that was highly active as a fungicide.

Other work has shown that when gum rosin is heated to 300°C for 15 minutes and the rosin distilled by either vacuum or steam, the pot residue amounts to about 20 to 25% of the starting rosin. This residue is apparently a crude dimer acid containing one carboxyl group. It has proven very useful in the preparation of mastics. Gum rosin was also modified by decarboxylation with phosphoric acid as a catalyst. The rosin oil obtained on treatment with fumaric acid gave a dibasic acid. Unsaturated polyesters were modified with this dibasic acid, mixed with styrene, and polymerized. The resulting laminating type plastic exhibited excellent solvent resistance.

Further progress was made in the research to develop diamines and diisocyanates from rosin derivatives for use in making polyurethane polymers and other industrial products. Methods were developed to prepare new amino alcohols, amino acids, diamines, dibasic acids, and diisocyanates from some potentially cheap resin acid derivatives. These methods should be adaptable to large scale use. Ways are being sought to eliminate undesirable side reactions in the preferred methods of synthesis, which involve five steps from pine gum to the diisocyanate. Completely hydrogenated rosin-derived diisocyanates can be prepared; they may be competitive with certain high-priced commercial diisocyanates.

2. Industrial Products from Rosin, Turpentine, and Pine Gum. Research on the preparation and evaluation of polyurethanes from polyols derived from rosin, resin acids, and pine gum was continued. When pure polyols derived from pine gum were incorporated at 5 to 50% levels in polyurethane elastomers, the resulting films had good polymer properties. The amount of diisocyanate required to produce the films varied inversely with the rosin incorporated--a potential economic advantage since the amount needed may be reduced as much as 20 to 40%. A similar trend has been observed

when a commercial product, the dark resin containing the color bodies removed in the refining of wood rosin, is used in rigid polyurethane foam. Incorporation of this dark resin results in a significant reduction in cost of the foam. Crude polyols available from this research should perform as well as or better than the commercial resin. The recent development of simple extraction procedures for isolating pure glycols from crude reaction products should stimulate industrial interest in the processes for making polyols.

In a contract project at Battelle Memorial Institute, about 30 new naval stores derivatives have been evaluated as components of commercial types of adhesive systems. These adhesives fall into four categories: pressure sensitive adhesives, rubber tackifiers, hot melts, and mastics. A number of these new materials have been found to be superior to products in commercial use today. Polyester products made from rosin modified with acrylic acid were found to be promising in the first three of these categories of adhesives. Additional derivatives will be evaluated.

Other contract work in progress at Battelle Memorial Institute is concerned with the evaluation of pine gum and rosin derivatives as additives for concrete. Materials to be evaluated have been obtained or prepared. A screening program is underway to determine which types of naval stores materials will be most effective for this end-use.

Publications - USDA and Cooperative Program

RPA 401 - NEW AND IMPROVED FOREST PRODUCTS

Chemical Composition, Physical Properties, and Structure

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AREA 7 - SWEET SORGHUM UTILIZATION

USDA and Cooperative Program

Problem Area		Scientist Man-Years (Estimated)		
No.	Title and Activity	Intra-mural	Extra-mural	Total
406	New and improved food products from field crops Chemical composition and physical properties	1.2		1.2
	TOTAL	1.2		1.2

Problems and Objectives

The Lower Rio Grande Valley, which is largely dependent on an agricultural economy, must have a greater selection of crops for diversification to meet unfavorable environmental and marketing conditions that frequently beset the area. One of the crops that have potential for providing profitable diversification is sweet sorghum, particularly since new disease-resistant varieties with high sugar content are now available. The modest water varieties with high sugar content are now available. The modest water requirements of sorghum and the subtropical climatic conditions conducive to an extended growing season also increase its attractiveness. In addition, integration of the processing of sorghum with that of beet and sugarcane would extend the use of costly installations in sugar factories. However, to achieve these goals, research is needed to develop practical methods for the recovery of sugar from sweet sorghum.

More specific objectives of the research are:

1. To identify major constituents and compositional changes that affect sugar recovery in relation to variety, cultural practice, environment, time of harvest, and handling after harvest.

2. To explore chemical and physical procedures for removing nonsugars from sweet sorghum juices.

3. To develop an economical process to recover the sugar from sweet sorghum.

4. To evaluate the processing characteristics of newer sorghum breeding lines grown under different agricultural practices.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Recovery of Sugar from Sweet Sorghum. Analytical evaluations of new sweet sorghum breeding lines and horticultural practices have provided information of value in developing new varieties and in determining crop management practices required for the use of the sorghums as a commercial sugar crop. Practical processing conditions were developed for eliminating essentially all of the starch and maximum amounts of other impurities that limit the quantity of raw sugar recoverable from sweet sorghum juices. Limited tests of these procedures indicated that they should be easily adaptable for use in raw cane sugar facilities. This research is conducted in cooperation with the Texas Agricultural Experiment Station and Crops Research.

Publications - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

None.

AREA 8 - RICE UTILIZATION

USDA and Cooperative Program

No.	Problem Area Title and Activity	Scientist Man-Years (Estimated) Intramural	 Extramural	 Total
406	New and improved food products from field crops Technology--process and product development	3.7		3.7
	TOTAL	3.7		3.7

Problems and Objectives

In the United States, the capacity for producing rice has increased faster than domestic consumption and exports. Detailed knowledge of chemical composition and physical properties of rices is needed to guide milling, processing, and product development. New and diverse food products that are economical to manufacture, convenient to prepare, and attractive in flavor and texture must be developed to increase the consumption of rice both domestically and abroad. Research is also needed to devise methods of treating rice to alter its cooking and processing characteristics for specific end uses.

Current objectives of this research are:

1. To identify the characteristics of the untreated or treated, whole or fractionated kernel that may be used to predict potential commercial uses.

2. To develop practical procedures for preventing or sealing checks and altering plasticity of rice kernels to improve milling yields.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Distribution of the Proteins. In research conducted under a P. L. 480 grant to Kyoto University, Japan, protein bodies were isolated from rice endosperm by differential centrifugation in a density gradient medium after mechanical or enzymic disintegration. The isolated protein bodies were easily broken in aqueous buffers and in high concentrations of ethanol. Electron microscopic examinations of these particles revealed that they were one to four microns in diameter and spherical or oval in shape and that some exhibited internal laminar structures consisting of alternating electron-dense and electron-thin layers. They are composed of proteins, about 60%; lipids, 23%; carbohydrates, 19%; phospholipids, 0.6%; phytic acid, 0.8%; RNA, 0.1%; nicotinic acid, 5/2 mg. %; and thiamine, trace amounts. Amylase and proteinase activities were observed in the protein bodies. The amino acid composition of rice endosperm did not differ from that of its protein bodies. Lysine is the limiting amino acid in each.

2. Composition and Properties of Rice Flours and Other Products. The physicochemical properties of isolated starches and their fractions from Belle Patna and Saturn varieties of rice were investigated to determine if processing characteristics could be predicted from these properties. Large differences were found in the intrinsic viscosities of amylopectins

from the outer surface (flour) and from the inner kernel (residue) of the Saturn variety. The gelatinization temperature range was significantly lower in starch from the peripheral flour than from the residue. These differences in the properties of the peripheral area may account for the greater cohesiveness of cooked medium-grain rices. No major differences were noted in the long-grain Belle Patna. Abnormally low viscosity for the peripheral flours was shown to be due to dilution by non-starch constituents. Mixtures of rice with cottonseed and peanut flours were extruder-cooked for use as a high protein (20%) precooked hot or cold breakfast cereal and finely ground for beverage use. These investigations were conducted in cooperation with the Louisiana Agricultural Experiment Station.

B. Technology--Process and Product Development

1. Increased Milling Yields. In new research, practical procedures are being devised to prevent or seal checks and to alter the plasticity of rice kernels. Achievement of this objective will increase the yield of rice obtained during processing.

Publications - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

Chemical Composition and Physical Properties

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